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Journal of Polymer Science, Part B

Polymer Letters

Editorial Board: R. M. Fuoss • J. J. Hermans • H. Mark • H. W. Melville • C. G. Overberger • G. Smets

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POLYMER LETTERS VOL. 1, PP. 201-205 (1963)

ATTEMPTED PREPARATION OF 2-DIETHYLPHOSPHONOETHYL ACRYLATES. AN UNEXPECTED REDUCTION PRODUCT*

The Michaelis-Becker reaction is frequently utilized to prepare phosphonates (1,2). This procedure involves the reaction of an alkyl halide, usually the bromide, with the sodium salt of an appropriate dialkyl hydrogen phosphonate according to the following scheme:

$$(RO)_2PONa + R'X \longrightarrow NaX + (RO)_2\overset{\overset{O}{\|}}{-P}-R'$$

Sodium diethyl phosphonate was prepared and reacted with 2-bromoethyl acrylate. Distillation after removal of solvent and salt, afforded a clear, colorless liquid, I, in 19% yield.

$$(EtO)_2PONa + CH_2{=}CH-\overset{\overset{O}{\|}}{C}-OCH_2CH_2Br \longrightarrow NaBr + I$$

A large fraction was found to be undistillable. The distilled product, however, exhibited no double bond absorption in the infrared and did not polymerize in the presence of azobisisobutyronitrile. Two possibilities presented themselves: (1) reduction of the double bond was taking place in the presence of unreacted sodium and diethyl phosphonate to give 2-diethylphosphonoethyl propionate, II; (2) the phosphonate had added across the conjugated double bond while hydrogenolysis of the bromine was taking place to give ethyl 3-diethylphosphonopropionate, III.

Reactions of dialkyl phosphonates with conjugated olefins are well known. Pudovik and others (3) have investigated reactions of this type.

Hydrogenolysis of secondary and tertiary bromides in the presence of sodium dialkyl phosphonates or trialkyl phosphites have been reported by Arbuzov (4). Thus, phenanthrene can be obtained from either 9-bromo- or 9,10-dibromophenanthrene by the use of either sodium diethyl phosphonate or triethyl phosphite. Reaction takes place merely by warming the mixture on a steam bath. Benzhydryl bromides react similarly. Chavane and Rumpf (5) reported the isolation of diethyl succinates in good yield when α-bromobutyrate was treated with sodium diethyl phosphonate. No normal product was obtained. A sodiumhalide interchange was suggested.

*Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

In order to determine which product was obtained, 2-diethylphosphonoethyl propionate, II, and ethyl 3-diethylphosphonopropionate, III, were prepared by the following reactions (3,6):

$$(EtO)_2\overset{O}{\overset{\|}{P}}H + CH_3CH_2\overset{O}{\overset{\|}{C}}-OCH{=}CH_2 \xrightarrow{AIBN} \underset{II}{CH_3CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_2\overset{O}{\overset{\|}{P}}(OEt)_2} \quad (1)$$

$$(EtO)_2\overset{O}{\overset{\|}{P}}H + CH_2{=}CH-\overset{O}{\overset{\|}{C}}-OCH_2CH_3 \xrightarrow{NaOEt}$$

$$\underset{III}{(EtO)_2\overset{O}{\overset{\|}{P}}CH_2-CH_2\overset{O}{\overset{\|}{C}}-OCH_2CH_3} \quad (2)$$

The physical properties are summarized in Table I.

TABLE I

Physical Properties of 2-Diethylphosphonoethyl Propionate (II) and Ethyl 3-Diethylphosphonopropionate (III)

Compound	b.p., °C.	n_D^{21}	Analysis[a] found		
			C	H	P
I	98-100 (0.2 mm.)	1.4302	45.15	8.17	12.82
II	136-138 (0.2 mm.)	1.4295	44.95	8.27	12.98
III	93-94 (0.7 mm.)	1.4291	45.21	8.58	12.68

[a]The calculated values are C, 45.37; H, 8.04; P, 13.08.

Although the infrared spectra of Compounds I, II, and III were very similar, several differences were readily observable. Both II and III showed absorption at 1350, 1372, 1390, 1428, and 1445 $cm.^{-1}$, however, differences in intensity were clearly exhibited. Compound II had rather broad absorption in the area around 800 $cm.^{-1}$ with small peaks at 792 and 805 $cm.^{-1}$ whereas III exhibited sharper absorption in this area with bands at 795 and 838 $cm.^{-1}$. Absorptions in the area from 950 to 1050 $cm.^{-1}$ were broader in II than in III. The spectrum of the Michaelis-Becker product, I, was identical in every respect to that of Compound III, thus providing strong evidences that it was ethyl 3-diethylphosphonopro-

pionate. The major infrared absorptions are listed in Table II.

TABLE II

Infrared Absorptions of 2-Diethylphosphonethyl Propionate (II) and Ethyl-3-Diethylphosphonopropionate (III)

Compound	C=O	C–O	P–O stretch	P–O–C in phase	P–O–C out of phase	P^{v}---O
I	1740	1185	1245	1030	1050	965
II	1740	1185	1250	1028	1045	970
III	1740	1185	1245	1030	1050	965

2-Diethylphosphonoethyl propionate, II, as well as several ω-dialkylphosphonoundecanoates were reported by Sasin et al. (6,7). The published infrared absorption are in agreement with the results reported here. It is of interest to note that McConnell and Coover (8) distinguished between 1-diethylphosphonoethyl acetate and 2-diethylphosphonoethyl acetate on the basis of infrared absorption. The 1-diethylphosphono compound had bands at 858, 800, 1047, and 1020 $cm.^{-1}$, while the 2-diethylphosphono compound showed absorption at 1031 and 793 $cm.^{-1}$ but lacked a band at 858 $cm.^{-1}$.

Compounds I and III were than hydrolyzed under similar conditions. Barium salts were prepared from the acids which were obtained. Elemental as well as infrared analysis indicated that both salts were identical. The major absorptions were at 1535, 1055, 1020, and 950 $cm.^{-1}$. Interestingly, no P=O absorption was found in the area around 1250 $cm.^{-1}$. Daasch (9) also reported the absence of this peak while investigating the infrared spectra of various salts of dialkyl phosphonates.

Ethyl 3-diethylphosphonopropionate was also formed while attempting to prepare 2-diethylphosphonoethyl propionate from triethyl phosphite and 2-bromoethyl acrylate using the Arbuzov procedure. Distillation gave a low yield of a liquid whose infrared spectra was identical to that of Compounds I and II.

Experimental*

Attempted Preparation of 2-Diethylphosphonoethyl Propionate (Michaelis-Becker Reaction). A procedure similar to that described by Finkelstein (2) was used. A sodium sand was prepared from 3.9 g. (0.17 g.-atom) of sodium in 300 ml. of toluene and 25.9 g. (0.19 mole) of diethyl

*Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

ylphosphonate was added dropwise. After the evolution of hydrogen had ceased, the toluene was cooled to 0°C. by means of an ice-bath, and 30.4 g. (0.17 mole) of 2-bromoethyl acrylate was slowly added. The solution was stirred overnight during which time a gelatinous precipiate formed. The filtrate was washed with three portions of saturated sodium bicarbonate and then dried over magnesium sulfate. The toluene was removed under vacuum and the remaining oil was distilled, affording 6.1 g. (15%) of a clear liquid, b.p. 92-95°C. (0.07 mm.); n_D^{25} 1.4309. The remaining product was undistillable. The distilled liquid was later identified as ethyl 3-diethylphosphonopropionate.

The reaction was then repeated using anhydrous ether as a solvent. From 6.0 g. (0.26 g.-atom) of sodium, 36.0 g. (0.25 mole) of diethyl phosphonate, and 44.8 g. (0.25 mole) of 2-bromoethyl acrylate, there was obtained 11.6 g. (19.5%) of a clear liquid, b.p. 98-100°C. (0.2 mm.); n_D^{21} 1.4302 (b.p. 123-124°C. (3 mm.); n_D^{20} 1.4310) (10).

ANAL. Calcd. for $C_9H_{19}O_5P$: C, 45.37; H, 8.04; P, 13.08. Found: C, 45.15; H, 8.17; P, 12.83.

Preparation of Ethyl 3-Diethylphosphonopropionate (III). This ester was prepared using a general method described by Pudovik and Arbuzov (3). To a solution of 37.5 g. (0.27 mole) of diethyl phosphonate and 26.0 g. (0.28 mole) of ethyl acrylate, there was added dropwise and with stirring, 10 ml. of a 10% solution of sodium in ethanol. The temperature rose to 100°C. on the addition of the sodium ethoxide. The solution was stirred overnight and then distilled to give 57.3 g. (88.5%) of a clear liquid, b.p. 93-94°C. (0.7 mm.); n_D^{21} 1.4291 (b.p. 123-124°C. (3 mm.); n_D^{20} 1.4310) (10).

ANAL. Calcd. for $C_9H_{19}O_5P$: C, 45.37; H, 8.04; P, 13.08. Found: C, 45.21; H, 8.58; P, 12.68.

Preparation of 2-Diethylphosphonoethyl Propionate (II). This compound was prepared by the method of Sasin et al. (6) except that azobisisobutyronitrile was used in place of t-butyl peroxide. From 34.5 g. (0.25 mole) of diethyl phosphonate and 25.0 g. (0.25 mole) of vinyl propionate, there was obtained 8.9 g. (15%) of a clear liquid, b.p. 136-138°C. (0.2 mm.); n_D^{21} 1.4295 (b.p. 103-104°C. (0.06 mm.); n_D^{30} 1.4291) (6).

ANAL. Calcd. for $C_9H_{19}O_5P$: C, 45.37; H, 8.04; P, 13.08. Found: C, 44.95; H, 8.27; P, 12.98.

Hydrolysis of the Michaelis-Becker Product. A solution of 5.2 g. (0.02 mole) of I and 20 ml. of a 10% potassium hydroxide solution was prepared by warming at 80°C. for 10 min. The solution was then heated at 100°C. for 30 min. Ethanol was evolved. After acidification with hydrochloric acid, the water was removed by distillation. The crude, hygroscopic solid which remained absorbed in the infrared at 1715 $cm.^{-1}$. The acid was dissolved in water and was made just basic to phenolphthalein with potassium hydroxide. A barium chloride solution was added and crystallization was induced by cooling and scratching. Filtration

afforded 2.5 g. of a barium salt which was washed several times with water, acetone and then ether.

ANAL. Calcd. for $C_3H_4O_5P\,Ba_{3/2} \cdot H_2O$: C, 9.61; H, 1.61; P, 8.26; Ba, 54.93. Found: C, 10.02; H, 1.86; P, 7.02; Ba, 54.09.

Hydrolysis of Ethyl 3-Diethylphosphonopropionate. Hydrolysis of 5.0 g. (0.02 mole) of this ester was accomplished as described above. A barium salt was obtained whose infrared spectrum was identical to that of the previously obtained salt.

ANAL. Calcd. for $C_3H_4O_5P\,Ba_{3/2} \cdot H_2O$: C, 9.61; H, 1.61; P, 8.26; Ba, 54.93. Found: C, 9.98; H, 1.60; P, 7.91; Ba, 54.11.

We gratefully acknowledge the assistance of the Department of the Army who supported this project under Contract Da–49–007–MD–557.

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POLYMER LETTERS VOL. 1, PP. 207-208 (1963)

PREPARATION AND POLYMERIZATION OF A NEW SILOXANE

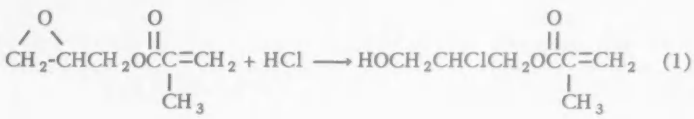
We wish to report the synthesis of a new monomer, containing both siloxane linkages and polymerizable methacrylate groups, by the reaction of one mole of allyltrichlorosilane with three moles of glycidyl methacrylate. The monomer is a clear, colorless liquid, stable without inhibitor at −10°C. Upon warming to 80°C., or upon the addition of a peroxide catalyst, it polymerizes to a transparent colorless, amorphous solid.

For example, 25.04 g. (0.175 mole) of glycidyl methacrylate were added from a dropping funnel over a half hour period to 10.25 g. (0.0584 mole) of allyltrichlorosilane in a three-necked flask equipped with a stirrer and thermometer. Cooling was required to keep the temperature below 55°C. The reaction was complete in about one hour, and the liquid product was stable, apparently indefinitely, at −10°C. without inhibitor. Addition of a few tenths of one per cent of 60% methyl ethyl ketone peroxide in dimethyl phthalate to a few grams of the monomer yielded a hard, glassy solid with the evolution of considerable heat.

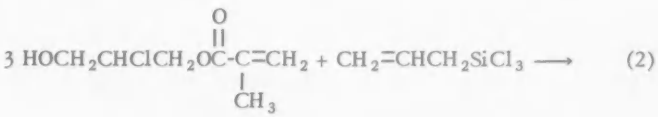
Vinyltrichlorosilane and 1,2-bis(trichlorosilyl)ethane also reacted with glycidyl methacrylate to form similar monomers and polymers.

It has been postulated (1) that the reaction of chlorosilanes with epoxides goes through an intermediate chlorohydrin, formed by the reaction of the epoxide with the HCl normally present in chlorosilanes. The chlorohydrin then reacts with the chlorosilane to form the siloxane plus HCl.

On this basis we write:



(1)



(2)

However, the reactions evidently do not go to completion. The monomer contains considerable readily-hydrolyzable chlorine, as determined by testing a water extract with silver nitrate. The epoxide absorption at 8.0 and 11.9 μ in the infrared spectrum of glycidyl methacrylate does not completely disappear from the spectrum of the monomer. Also, while the expected molecular weight of the monomer is 604, the value determined in benzene by a Mechrolab "Osmometer" (2) is 555.

The monomer evidently polymerizes by addition, since a polymer sample, finely powdered and vacuum dried to remove all volatiles, gave an elemental analysis is good agreement with the values calculated for the monomer. Polymerization is accompanied by a decrease in infrared absorption at 6.10,7.70, and 12.35 μ; bands associated with the carbon-carbon unsaturation.

Polymerization of the tetraunsaturated monomer yields an apparently highly crosslinked system; the polymer is insoluble in common solvents, is amorphous, and does not melt below its decomposition point. As determined by thermogravimetric analysis (3), it begins to decompose at about 250-300°C. Employing the procedures of Warfield and Petree (4), no glass transition was detected up to about 180°C. Characterization of the polymer by electrical resistivity techniques (4,5) also indicates a high degree of crosslinking.

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POLYMER LETTERS VOL. 1, PP. 209-213 (1963)

EFFECT OF STEREOREGULARITY ON THE GLASS TEMPERATURES OF A SERIES OF POLYACRYLATES AND POLYMETHACRYLATES

Density measurements and x-ray fiber data on poly(methyl methacrylate) polymerized in hydrocarbon solution using certain anionic initiators were reported in a previous paper (1). From these results it was concluded that the polymers contained chains having isotactic sequences of configuration. Other polymerizations of this monomer, either free-radically at low temperatures or anionically in highly solvating media such as 1,2-dimethoxyethane, yielded polymers which had physical properties differing substantially from those of the isotactic polymers, even when compared in their noncrystalline states. Orientation of crystallites in these non-isotactic polymers was not achieved; however, on the basis of high temperature solution NMR spectra, they were thought to be highly syndiotactic (2).

The previously reported results of dilatometric measurements (3) on these polymers, as well as those of the conventionally prepared polymer, are presented in Table I.

TABLE I

Properties of Polymers of Methyl Methacrylate

Type designation	Glass temp., °C.	m.p., °C.	Density of amorphous polymer at 30°C., g./ml.	Presumed chain configuration
I	115	(>200)	1.19	syndiotactic[a]
II	45	160	1.22	isotactic[a]
Conventional	104	--	1.188	essentially syndiotactic

[a]The configurations originally presumed for Type I and II were the reverse of those shown here. The present assignments are believed to be correct.

The T_g of the conventional poly(methyl methacrylate) is evidently much closer to that of the syndiotactic than to the isotactic polymer. This result, together with the infrared data (4), nuclear magnetic resonance (NMR) spectra (2) and gel melting point determinations (5) indi-

TABLE II

Glass Temperatures (°C.) of Polymethacrylates

Polymer	Method of polymerization		
	Free-radical at near-ambient temp.[a]	Free-radical at low temp.[b]	Anionic in non-polar solvent
Methyl methacrylate	104	115 to 122	43 to 50
Ethyl methacrylate	66	—	8 to 12
Isopropyl methacrylate	81	85	27
Butyl methacrylate	19	—	−24
Isobutyl methacrylate	53	—	8
Cyclohexyl methacrylate	66	—	51
Isobornyl methacrylate	—	111	110

[a] 44 to 60°C.
[b] t ≤ −30°C.

TABLE III

Glass Temperatures (°C.) of Polyacrylates

Polymer	Method of polymerization		
	Free-radical at near-ambient temp.[a]	Free-radical at low temp.[b]	Anionic in non-polar solvent
Methyl acrylate	8	—	10
Ethyl acrylate	−24	−24	−25
Isopropyl acrylate	−3 to −6	−2 to 11	−11
Sec-butyl acrylate	−22	−20	−23
Tert-butyl acrylate	43	40	40
Cyclohexyl acrylate	19	16	12
Isobornyl acrylate	94	96	90

[a] 44 to 60°C.
[b] t ≤ −30°C.

cates that the polymer prepared by conventional techniques contains an appreciable fraction of monomer units in syndiotactic sequences, possibly as high as 70 to 80%.

These results are contrary to those reported for other polymers obtainable in different stereoisomeric forms (6-9) where no significant differences were observed between the conventional and the stereoregular forms. Natta and co-workers (6), for example, observed a glass transition at 90°C. for both isotactic and atactic polystyrene by dilatometric methods. Newman and Cox (7) from their heat distortion measurements observed no large effects of stereospecificity on the T_g of polystyrene or of polypropylene in the unannealed, unstretched state. Natta and coworkers (9), reporting dilatometric results on a homologous series of poly-α-olefins, also concluded that the T_g in all cases was practically independent of the stereoisomorphic structure. Our results with poly(methyl methacrylate), however, have since been verified by the dielectric measurements of Mikhaelov and Borisova (10) and the dynamic mechanical measurements of Gall and McCrum (11). In both cases the glass transitions obtained from the dispersion maxima showed differences between the isotactic and syndiotactic polymers comparable to those found dilatometrically.

Since the dilatometric results on poly(methyl methacrylate) were reported, the dependence of T_g on polymerization conditions has also been observed in some higher alkyl methacrylates polymerized in this company by the same general techniques used for the preparation of the methyl methacrylate polymers. An analogous series of polyacrylates has also been prepared, but shows no significant dependence of T_g on the method of polymerization.

The results of dilatometric measurements on seven amorphous, unoriented polymethacrylates, classified according to general method of polymerization, are shown in Table II. Free-radical polymerization at near-ambient temperatures (second column) normally results in the so-called "conventional" poly(methyl methacrylate). Free-radical polymerizations at low temperatures (third column) lead to Type I poly(methyl methacrylate) while anionic polymerizations in organic solvents of the type used here (fourth column) have, in the past, resulted in Type II poly(methyl methacrylate). Larger differences in T_g are observed between polymers of the same chemical species in the lower members of the series. As the size of the alkyl group attached to the ester increases however, these differences in T_g decrease. Thus, while there is a T_g difference of almost 80° between the syndiotactic and isotactic forms of poly(methyl methacrylate) there is no distinguishable T_g difference between the different samples of poly(isobornyl methacrylate) prepared under analogous conditions.

Seven polyacrylates were studied (Table III). With the exception of poly(isopropyl acrylate), where an overall variation of 22° is observed,

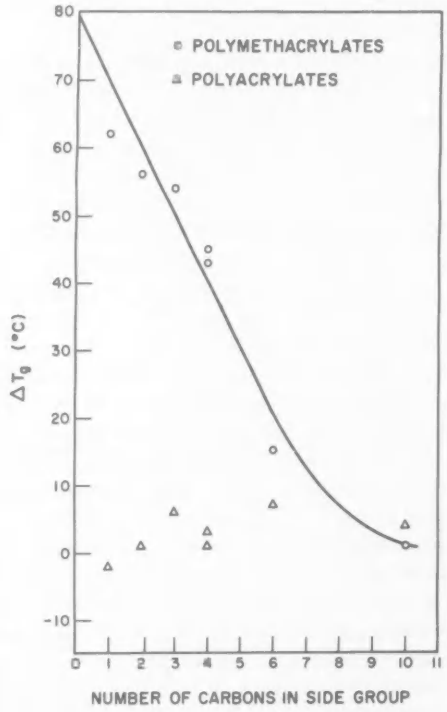

Fig. 1. Dependence of ΔT_g (T_g conventional $- T_{g\ Type\ II}$) of acrylate and methacrylate polymers on the number of carbon atoms in the alkyl side group. (For poly[isobornyl methacrylate] the Type I was substituted for the conventional polymer, which was not available).

there appears to be little or no relationship between polymerization conditions and the T_g of the polymer.

In Figure 1, values of ΔT_g (the difference between the T_g of the conventionally prepared polymer and that of the corresponding Type II polymer) have been plotted as a function of the number of carbon atoms in the alkyl ester group. The scatter in the data is not unreasonable, since in addition to the usual error (ca. ±2°) in the dilatometric technique, some of the ester groups are linear and others are branched or cyclic. Moreover, it is unlikely that all conventionally prepared polymers have the same degree of syndiotacticity or that all of the Type II polymers have the same degree of isotacticity.

In relating T_g to structure, the relative importance of inter-chain and nearest-neighbor intra-chain interactions and the exact manner in which they determine the T_g is still controversial generally, and probably varies with different systems. In the polymethacrylates it is assumed that

the higher members of the series, when polymerized under certain conditions, have the same type of stereo structure as poly(methyl methacrylate) polymerized under those conditions. We must conclude then that since large differences in T_g are observed for polymers which are otherwise chemically identical, the manner of placement and the resultant effect on the interaction between adjacent units in the chain have a considerable effect on the T_g. We would then expect the total interaction between adjacent units per unit volume to become smaller as the size of the pendant groups, which are further from the back-bone is increased. This is what we observe. In the polyacrylates, the much smaller differences in T_g resulting from differences in tacticity can be explained by the greater freedom of rotation in the backbone because the α-methyl group is absent. Differences in tacticity would have less tendency to enforce preferred conformations on the chain and would therefore have less effect on chain flexibility.

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POLYMER LETTERS VOL. 1, P. 215 (1963)

A NEW AND CONVENIENT SYNTHESIS OF POLY(VINYL ESTER)S

Poly(vinyl ester)s are produced by two main routes; namely the polymerization of vinyl esters and the esterification of poly(vinyl alcohol). If the side chain of poly(vinyl ester) has an unsaturated bond, the synthetic method will be the latter only. The usual method of the esterification of poly(vinyl alcohol) is the condensation of hydroxyl groups of polymer and acid halides in dry pyridine at the elevated temperature. In this process (1) the moisture must be strictly excluded, and the reaction time is very long (28 hr. or so).

The new method proposed in this letter is one of the Schotten-Baumann reaction, therefore, the reaction is fast and the moisture has no effect. One volume of 1 mole/liter aqueous poly(vinyl alcohol) solution (mole number on the hydroxyl group), one volume of 4 mole/liter aqueous sodium hydroxide solution, and one volume of methyl ethyl ketone are mixed and cooled. Cinnamoyl chloride (1.2 equiv. to poly(vinyl alcohol)), 1.16 volume of methyl ethyl ketone, and 0.24 volume of toluene are mixed and cooled. The two solutions are mixed in the vessel open to air, and agitated for 90 min. below 5°C. The reaction mixture separates into two layers after the agitation ceases. The produced poly(vinyl cinnamate) is contained in the organic solvent layer (the upper layer) and the yield is about 95%. This method appears far superior in convenience and yield to the other reported method for the esterification of poly(vinyl alcohol) – the reaction in dry pyridine. It will offer one of the industrial process for the production of poly(vinyl ester)s.

Detailed reports on this method will be published in near future.

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POLYMER LETTERS VOL. 1, PP. 217-221 (1963)

SPHERULITES OF POLY-(4-METHYL-PENTENE-1)

It is well known that the polymer prepared from 4-methyl-pentene-1 by stereospecific polymerization is highly crystalline (1-3). Though the kinetics of isothermal crystallization in this polymer by dilatometry have been reported (4), the spherulitic structures have not been investigated. The degrees of crystallinity of poly-(4-methyl-pentene-1) are lower than those of polypropylene owing to the difference between their chemical structures.

It could be expected that a polymer with high stereospecificity could form spherulites from the solution as well as from the melt. This brief report is concerning the spherulitic structures of poly-(4-methyl-pentene-1) which polymerized by $Al(C_2H_5)_3$–$TiCl_3$ catalyst.

The polymer was extracted by the use of n-heptane in a Soxhlet-extractor. The extract-residues were molten between two glass surfaces in a form of thin film at 280°C. for 3 min. and crystallized slowly. The amount of residue decreased with extraction time as shown in Figure 1.

The spherulitic structures were observed by phase contrast microscopy. The more the specimens were extracted, the more nearly perfect were the spherulites formed, as shown in Figure 2. We could not observe the spherulites of poly-(4-methyl-pentene-1) by crossed polaroid microscopy because of the decrease in birefringence.

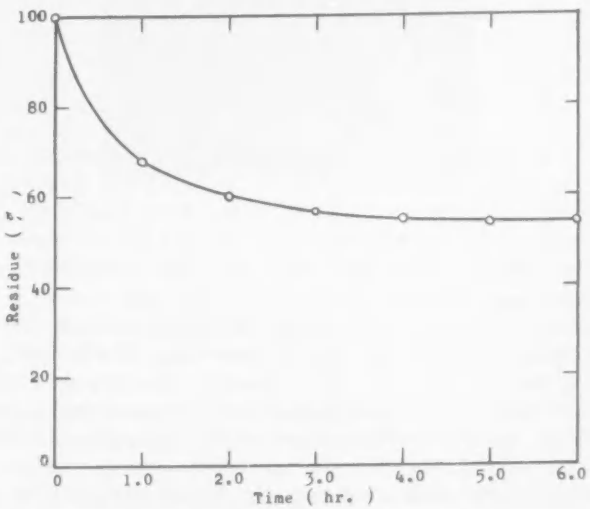


Fig. 1. Extraction by n-heptane.

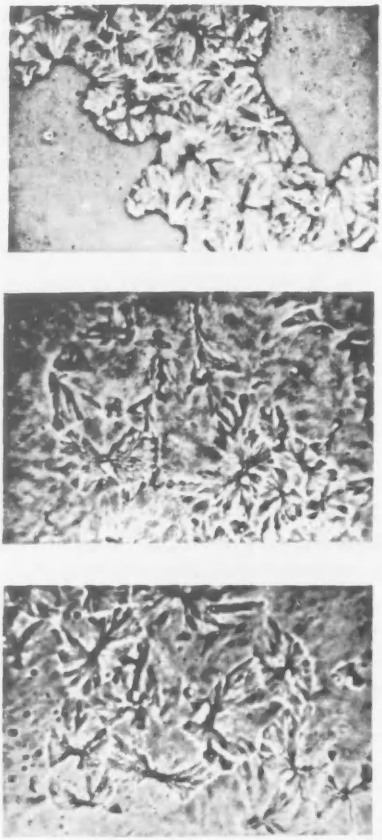


Fig. 2. Change of spherulitic structures by n-heptane extraction. 400×. (top) 1 hr. extraction; (middle) 3 hr. extraction; (bottom) 4 hr. extraction.

The polymer specimens which were thoroughly extracted by n-heptane for several hours yielded spherulites with sheaflike structures when viewed by phase contrast microscopy, as shown in Figure 3. Figure 4 shows more detailed pictures of the spherulites. The nuclei are composed of numerous sheaves. The spherulites probably grow through sheaf-intermediates and the regular branching mechanism proposed by Keller (5). Similar sheaflike structures have been observed in the spherulites of nylon 6 from formic acid solution (6), nylon 610 from a mixed solvent of benzyl alcohol-m-cresol (5), and polyethylene from solution (7,8), and polyoxymethylene (9).

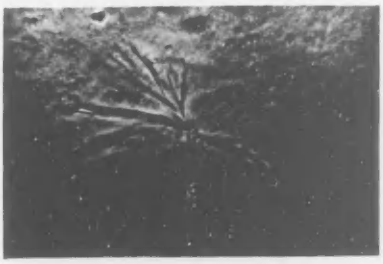
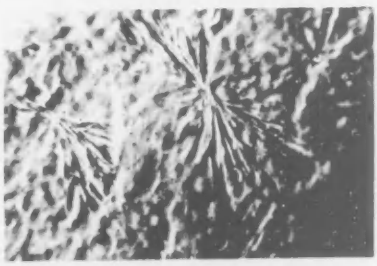


Fig. 3. Sheaflike structure of poly-(4-methyl-pentene-1) spherulite. 900×.



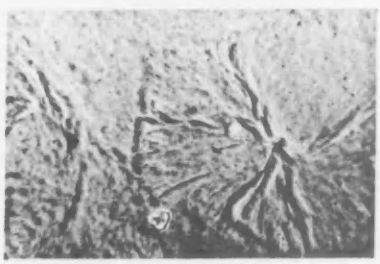


Fig. 4. Sheaflike structure of poly-(4-methyl-pentene-1) spherulites by phase contrast microscopy. 900×. (top) Symmetrical sheaf; (bottom) asymmetrical sheaf.

In our previous reports (10, 11) we showed the dendritic spherulites in polypropylene. We did not observe sheaflike structures in polypropylene spherulites either by crossed polaroid and phase contrast microscopy.

Figure 5 shows the regular branching of spherulites in thin films (below 10 μ thickness) from poly-(4-methyl-pentene-1). The overlapping of sheaves and branches is observed in Figure 6.

The results of observations on spherulites by many investigators have given us the concept that the composing units of spherulites are sheaf-

Fig. 5. Branching of sheaf by phase contrast microscopy. 900×.

Fig. 6. Overlapping of sheaf by phase contrast microscopy. 430×.

like fibrils when spherulites are formed from the solution and are lamellae when they are crystallized from the melt (12). Geil (9), however, showed that nuclei with sheaflike-fibrous structures in polyoxymethylene spherulites from the melt are composed of numerous lamellae. Further, he has observed that the nuclei of spherulites in branched polyethylene grown from a thin molten film have a sheaflike structure and that each sheaf is composed of numerous lamellae (8).

The spherulites in poly-(4-methyl-pentene-1) from the melt have sheaflike fibrous structures which could be composed of lamellae, when observed by phase contrast microscopy.

The author is indebted to Mr. Y. Atarashi for preparing the poly-(4-methyl-pentene-1) polymer used.

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THE GLASS TEMPERATURE OF RANDOM ADDITION COPOLYMERS

Several relationships (1-4) have been proposed for the purpose of obtaining the glass temperature of a copolymer from the glass temperatures of its constituent homopolymers. These expressions differ primarily in the assignment and physical identification of the weighting parameters used in the averaging process. They have in common the fact that they do not take into account any contribution that may arise from an A–B interaction.

On the basis of this, the following relationship is proposed for random addition copolymers:

$$T_g \text{ copolymer} = X_A^2 T_A + X_B^2 T_B + 2X_A X_B T_{AB} \text{ in } ^\circ K. \qquad (1)$$

where X_A and X_B are the mole fractions of A and B units in the copolymer, T_A and T_B are the glass temperatures of the respective homopolymers, and T_{AB} is the glass temperature of the 50–50 alternating copolymer (if this is not available, a reasonable approximation is given by the term $(T_A T_B)^{1/2}$).

The relationship may also be extended to random stereospecific polymers, where the glass temperature of an atactic polymer is given in terms of the glass temperatures of the isotactic and syndiotactic homopolymers. In this case, A and B are replaced by d and l, $X_d = X_l = 0.5$, $T_d = T_l$ is the glass temperature of the isotactic polymer, and T_{dl} is the glass temperature for the corresponding syndiotactic polymer. It is thus seen that the glass temperature of the atactic polymer should be the arithmetic mean of the isotactic and syndiotactic glass temperatures.

It is acknowledged that part of this work was conceived at Brown University while the author was on a postdoctorate fellowship with Prof. J. H. Gibbs.

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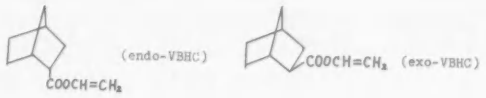
RADICAL POLYMERIZATION OF endo- OR exo-VINYL BICYCLO [2.2.1]-HEPTANE-2-CARBOXYLATE

Recently, several studies on the polymerization and copolymerization of the monomers containing bicyclo [2.2.1]-heptene or heptadiene ring have been seen in literature (1-6). In order to clarify the effect of bicyclo [2.2.1]-heptane ring on the radical polymerization, we prepared endo- and exo-vinyl bicyclo [2.2.1]-heptane-2-carboxylates (endo- and exo-VBHC) and made a kinetic study on their radical polymerization.



endo- or exo-Bicyclo [2.2.1]-heptane-2-carboxylic acid was synthesized from cyclopentadiene and acrylic acid (7) or methyl acrylate (8) by Diels-Alder's reaction and followed by hydrogenation. Pure endo- or exo-VBHC was then prepared by the ester-interchange reaction of corresponding acids with vinyl acetate.

endo-VBHC: b.p. 81-82°C./10 mm. Hg, d_4^{16} 1.0206, n_D^{20} 1.4775

exo-VBHC: b.p. 83.0-83.5°C./10 mm. Hg, d_4^{16} 1.0243, n_D^{20} 1.4778

Polymerizations were carried out in benzene at 50-70°C., using 2,2′-azobisisobutyronitrile (AIBN) as an initiator. Both monomers easily polymerized with no induction period, while the exo-monomer polymerized faster than the endo-monomer. The results are shown in Table I. In this table, overall activation energies and frequency factors are also tabulated.

As can be seen from Table I, the activation energies of the exo- and endo-monomers were the same, but the frequency factors differed. This result might indicate that the difference in rate arose from the steric effect of endo-bicyclo [2.2.1]-heptane ring. From the kinetic measurements, the same rate equation was derived for both monomers as follows:

$$R_p = k[AIBN]^{0.5}[VBHC]^{1.8}$$

Table II shows the intrinsic viscosities, $[\eta]$ (dl./g.), of both resulting polymers. The intrinsic viscosity of the polymer obtained from the exo-VBHC, which polymerized faster than the endo-monomer, was also higher than the polymer of endo-VBHC. These results might support the steric

TABLE I

Polymerization Constants of endo- and exo-VBHC

Monomer		endo-VBHC	exo-VBHC
$R_p \times 10^5$ (mole/liter, sec.)[a]	50°C.	1.20	1.59
	55°C.	2.32	2.92
	60°C.	4.68	5.50
	65°C.	8.04	10.0
	70°C.	14.3	16.8
E (kcal./mole)		26.7	26.8
A (mole/liter, sec.)		1.74×10^{13}	2.51×10^{13}
ΔS^a (cal./mole, deg.)		1.83	2.58

[a][AIBN] = 6.41×10^{-3}, [endo-VBHC] = 3.074, [exo-VBHC] = 3.082 mole/liter.

TABLE II

Intrinsic Viscosities of Polymers of exo- and endo-VBHC (in Benzene at 30°C.)

Monomer concn. in polymerization[a]	Poly-endo-VBHC	Poly-exo-VBHC
6.13	0.080	0.161
6.13[b]	0.096(120)[c]	0.235(460)[c]
4.30	0.072	0.145
3.07	0.074(140)[c]	0.142
1.85	0.073	0.123
1.23	0.075	0.122

[a]Polymerizations were carried out in benzene at 60°C.: [AIBN] = 6.41×10^{-3} mole/liter.

[b]Polymerizations were carried out by photo at −30°C.: [AIBN] = 6.4×10^{-2} mole/liter.

[c]These values are the degrees of polymerization of polyvinyl alcohol obtained by hydrolysis.

effect in the endo-VBHC mentioned above. As understood from Table II, the values of $[\eta]$ were very small. This result was confirmed from the molecular weight determination of polyvinyl alcohol obtained after hydrolysis, as shown in Table II. Since the bicyclo [2.2.1]-heptane group con-

tains a number of active hydrogen atoms, it is clear that the effective chain transfer to monomer is very important. This fact is characteristic of radical polymerization of the monomers containing the bicyclo[2.2.1]-heptane ring.

Copolymerizations of both endo- and exo-monomers (M_2) with styrene (M_1) were carried out at 60°C. From the composition analyses of the resulting copolymers, monomer reactivity ratios were determined as $r_1 = 30$, $r_2 = 0.01$. These values were in agreement with the values for the copolymerization of vinyl acetate with styrene ($r_1 = 55 \pm 10$, $r_2 = 0.01 \pm 0.01$). Accordingly, it was concluded that the endo- or exo-bicyclo [2.2.1]-heptane group in VBHC monomer showed nearly the same effect as the methyl group in vinyl acetate.

Both polymers obtained from endo- and exo-VBHC were colorless powder and melted at 90-105°C. These polymers were soluble in benzene, ethyl ether, tetrahydrofuran, carbon tetrachloride, and ethyl acetate, but insoluble in methanol, ethanol, acetone, dimethyl formamide, and petroleum ether. An atactic and low molecular weight polyvinyl alcohol was obtained by the hydrolysis of both polymers.

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THE AMOUNT OF HOMOPOLYMER FRACTIONS IN LINEAR RANDOM COPOLYMERS HAVING THE MOST PROBABLE MOLECULAR WEIGHT DISTRIBUTION

In a copolymer system the probability P that a unit chosen at random is an A unit is given by the mole fraction of A units X_A. The probability that this unit is a member of a sequence of n units is represented by

$$P_n = X_A p_0^{n-1} \tag{1}$$

In this equation p_0 represents the probability that an A unit is succeeded by another A unit. In random copolymers this probability is independent of the number of A's preceding the given A unit in the sequence and is equal therefore to X_A. Hence we obtain:

$$P_n = X_A^n \tag{2}$$

The weight fraction of n-mers built only from A units $w_{A,n}$ in a linear random copolymer system having the most probable distribution is thus given by

$$w_{A,n} = n(1-p)^2 p^{n-1} X_A^n \tag{3}$$

In eq. (3), p stands for the probability that a particular reactive group

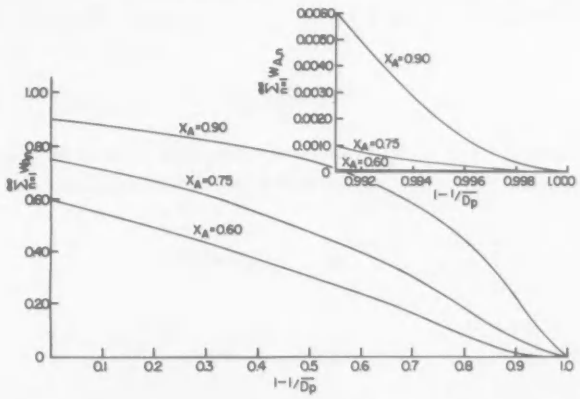

Fig. 1. Weight fractions of homopolymer in a linear random copolymer system having the most probable molecular weight distribution as functions of $1 - 1/\overline{Dp}$, when $M_A = M_B$.

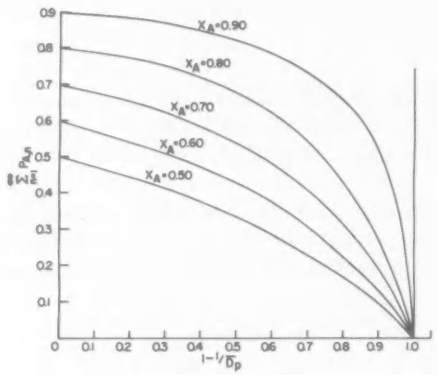

Fig. 2. Mole fractions of homopolymer in a linear random copolymer system having the most probable molecular weight distribution as functions of $1 - 1/\overline{Dp}$.

has reacted. For a system where all molecules are bifunctional, this probability is equal to

$$p = 1 - (N/N_0) \tag{4}$$

In eq. (4), N_0 equals the number of molecules at the start of the reaction, while N stands for the number of molecules at the end of the reaction. In the derivation of eq. (3) it has been assumed that both units have the same molecular weight.

The maximum weight fraction of n-mers built from A units only is obtained from eq. (3) by placing

$$n = -\frac{1}{\ln (X_A p)} \tag{5}$$

The weight fraction of all molecules containing A units only is obtained by summation of $w_{A,n}$ over the entire molecular length range.

$$\sum_{n=1}^{\infty} w_{A,n} = \sum_{n=1}^{\infty} n(1-p)^2 p^{n-1} X_A{}^n$$

$$= (1-p)^2 X_A \sum_{n=1}^{\infty} n(pX_A)^{n-1} \tag{6}$$

$$= \frac{(1-p)^2 X_A}{[(1-p)X_A]^2}$$

Weight fractions of homopolymer molecules for copolymer systems having an initial mole fraction of A units equal to 0.90, 0.75, and 0.60 and $M_A = M_B$ are shown in Figure 1 as functions of $1 - (1/\overline{Dp})$, where $\overline{Dp}$ = the average degree of polymerization.

The probability p_n that a molecule selected at random is composed of n units of species A is given by

$$P_{A,n} = p^{n-1}(1 - p)X_A{}^n \tag{7}$$

The summation of $P_{A,n}$ over the entire range of n yields the mole fraction of all molecules containing A units only.

$$\sum_{n=1}^{\infty} P_{A,n} = \sum_{n=1}^{\infty} p^{n-1}(1 - p)X_A{}^n$$

$$= (1 - p)X_A \sum_{n=1}^{\infty} (pX_A)^{n-1} \tag{8}$$

$$= \frac{X_A(1 - p)}{(1 - p)X_A}$$

The mole fractions of homopolymers for the copolymer compositions $X_A = 0.9$, 0.8, 0.7, 0.6, and 0.5 as functions of the degree of polymerization are represented in Figure 2.

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POLYMER LETTERS VOL. 1, PP. 233-236 (1963)

DIMENSION OF POLYVINYL CHLORIDE IN FLORY THETA SOLVENT

The properties of dilute solution of polyvinyl chloride have been extensively studied by many authors. However, we are not aware of any experimental work carried out under the unperturbed state for polyvinyl chloride. This investigation was initiated with the intention of studying the relationship between the molecular dimension and polymerization temperature of polyvinyl chloride. In the present paper, we will report the unperturbed dimension of ordinary polyvinyl chloride as a part of the investigation.

The polyvinyl chloride employed in this work was prepared by the ordinary suspension polymerization method with lauroyl peroxide at 50°C. and it was fractionated at 30°C. by conventional precipitation technique; the solvent was tetrahydrofuran and the precipitant water. The weight-average molecular weight, $\bar{M}_w$, of each fraction was determined from the light-scattering results on tetrahydrofuran solutions.

After a number of preliminary experiments, we found that benzyl alcohol was a theta solvent for polyvinyl chloride. The temperatures, T_p, at which the phase separation occurred on cooling the benzyl alcohol solutions of the fractions are shown in Figure 1 as a function of polymer concentration. The critical miscibility temperature, T_c, corresponding to the maximum point in the curve are related to the molecular weight by the following eq. (1):

$$1/T_c = (1/\theta)[1 + (b/\bar{M}_w^{1/2})] \qquad (1)$$

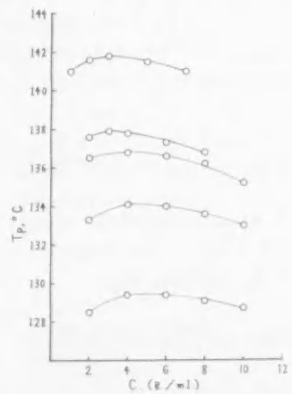

Fig. 1. Phase separation temperature, T_p, of five fractions of polyvinyl chloride as a function of polymer concentration in benzyl alcohol.

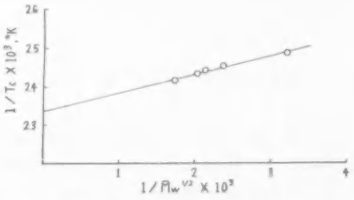

Fig. 2. Reciprocal critical miscibility temperature, T_c, against reciprocal square root of molecular weight of five fractions of polyvinyl chloride in benzyl alcohol.

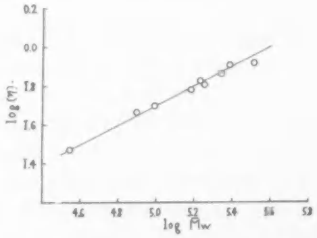

Fig. 3. Logarithmic plot for intrinsic viscosity at theta temperature in benzyl alcohol against molecular weight of fractions of polyvinyl chloride.

where b is a constant characteristic of a given polymer-solvent system. The theta temperature, θ can be obtained from the intercept in the plot of $1/T_c$ versus $1/M^{1/2}$ as shown in Figure 2. The value obtained by this method was 155.4°C.

The intrinsic viscosity, $[\eta]_\theta$, at theta temperature was obtained for each fraction, and log $[\eta]_\theta$ was plotted against log $\bar{M}_w$ as shown in Figure 3. $[\eta]_\theta$ was quite accurately proportional to $\bar{M}_w^{1/2}$ as represented by eq. (2).

$$[\eta]_\theta = 1.56 \times 10^{-3} \bar{M}_w^{1/2} \tag{2}$$

Assuming $\Phi = 2.1 \times 10^{21}$, we calculated the values of the root mean square end-to-end distance, $(\bar{r}_0^2)^{1/2}$, of the polymer chain in the unperturbed state from Flory's eq. (3) (ref. 1).

$$[\eta]_\theta = \Phi (\bar{r}_0^2/M)^{3/2} M^{1/2} \tag{3}$$

The result was

$$(\bar{r}_0^2)^{1/2} = 9.06 \times 10^{-9} M^{1/2} \tag{4}$$

TABLE I

Comparison of Unperturbed Molecular Parameters on Various Polymers

Polymer	θ, °C.	$(\bar{r}_0^2/P)^{1/2} \times 10^8$	$(\bar{r}_0^2/\bar{r}_{0f}^2)^{1/2}$	Ref.
Polymethyl methacrylate	25.0	4.88	2.24	(2)
Poly-n-octyl methacrylate	16.8	4.99	2.32	(2)
Polyisobutylene	24.0	5.95	1.93	(3)
Polystyrene	25.0	6.81	2.14	(4)
Polyvinyl acetate	26.5	7.01	2.28	(5)
Polycyclohexyl methacrylate	23.0	7.05	2.29	(6)
Polyvinyl chloride	155.4	7.16	2.32	
Poly-n-lauryl methacrylate	13.0	7.80	3.58	(2)
Polyvinyl benzoate	32.5	8.15	2.65	(7)

The quantities, $(\bar{r}_0^2/P)^{1/2}$ and $(\bar{r}_0^2/\bar{r}_{0f}^2)^{1/2}$ were also calculated as the measure of extension of polymer chain; where P is the degree of polymerization and $(\bar{r}_{0f}^2)^{1/2}$ denote the root mean square end-to-end distance calculated for free rotation assuming 1.54 A. for the C–C bond length and 109.5° for the C–C–C bond angle. The values of $(\bar{r}_0^2/P)^{1/2}$ and $(\bar{r}_0^2/r_{0f}^2)^{1/2}$ of the results were listed in Table I, together with those for other polymers (2-7).

As shown in Table I, the degree of extension of polyvinyl chloride is larger than that of both polystyrene and polyvinyl acetate. Unfortunately, the theta temperature for polyvinyl chloride is very much higher than those for other polymers and we could not compare the chain dimension at the same temperature. However, it is likely that the value for polyvinyl chloride will become much larger than others when the comparison was made at a given lower temperature, as we may expect that the unperturbed dimension of a polymer molecule will decrease with increasing temperature.

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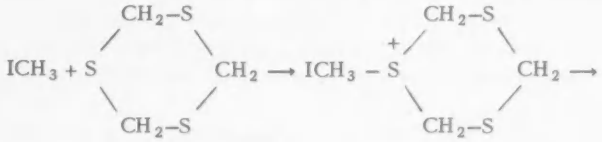
POLYMERIZATION OF TRITHIANE

During the course of investigating the polymerizability of 5- and 6-membered cyclic sulfides and sulfones, s-trithiane was polymerized to polymethylene sulfide. Although polymethylene sulfide has been prepared, (1,2) it has not hitherto been polymerized from the corresponding cyclic monomer.

Trithiane is a stable, crystalline solid, melting at 215–216°C. The conformation of the s-trithiane ring is very interesting, since there is no possibility of hydrogen eclipse, even in the boat form which predominates (3,4).

We have found that cationic catalysts (e.g., boron fluoride, methyl iodide, antimony (III) fluoride, and dimethyl sulfate) polymerize the anhydrous trithiane to linear polymethylene sulfide probably via a mechanism similar to the polymerization of trioxane or formaldehyde (5,6).

A stable sulfonium complex is assumed to be formed between the catalyst and the cyclic sulfide. This complex undergoes a slow, spontaneous reaction followed by ring opening to give a resonance-stabilized carbonium ion as the propagating species:



The polymerization has been found to take place, preferably in bulk, at 220–230°C. No polymerization was observed to occur in solution with these same catalysts. Further work to find suitable nonpolar solvents for this reaction is in progress.

Experimental

Polymerization of s-Trithiane. Into a dry 200-mm. × 25-mm. Pyrex polymerization tube fitted with sidearm and gas-inlet capillary which extended to the bottom of the tube was added 7.0 g. (0.050 moles) trithiane. The tube was lowered into a molten wax bath and the contents were heated to 225°C. under a nitrogen stream. When the trithiane had become completely liquefied, 0.007 g. boron fluoride gas was passed in-

to the melt through the capillary tube. The mixture immediately became very viscous. The polymerization was stopped after 35 min. A hard, brittle solid was removed from the tube, pulverized, and extracted with boiling benzene to remove unreacted trithiane. The yield of the vacuum-dried, light tan material was 5.2 g. (90%). The polymer had a melting range of 245–260°C. (The literature records melting points of 123–124° (7), 175–176° (2,8), and 220–245°C. (1), which may be attributable to differences in the degree of polymerization.) The polymer was oxidized to polymethylene sulfone in formic acid solvent with 30% hydrogen peroxide at 70–80°C.

ANAL. Calcd. for $(-CH_2S-)_n$: C, 26.08; H, 4.35; S, 69.57. Found: C, 25.87; H, 4.74; S, 69.86.

Properties. The infrared spectrum of the polymer showed the following absorption peaks: CH_2 deformation: 7.4 and 8.5 μ, strong; 11.5μ, moderate; 13.5 and 14.15 μ, strong. The polymers were insoluble in most common organic solvents except α-bromonaphthalene and a solvent mixture of tetramethylene sulfone and α-chloronaphthalene above 210°C. When these solutions were cooled, the polymers precipitated. The inherent viscosity of the polymers was determined at 230°C. in α-bromonaphthalene.*

TABLE I

Viscosity Data for Polymethylene Sulfide Polymers

Catalyst used to prepare sample	Viscosity, centistokes at 232.2°C., at three concentrations of α-$C_{10}H_7Br$[a]			Inherent viscosity, centistokes
	2%	1.5%	0.7%	
BF_3	0.459	0.445	0.459	0.050
$(CH_3)_2SO_4$	0.464	0.456	0.430	0.047
CH_3I	0.439	0.430	0.420	0.014

[a]For the reference liquid α-bromonaphthalene, viscosity at 232.2°C. was 0.416 centistokes; refractive index at 20° was 1.6565.

*Viscosities were determined by the Schwartzkopf Microanalytical Laboratory, Woodside, N. Y., at three concentrations: 0.7, 1.5, and 2.0%.

Thermal Stability. Purified polymethylene sulfide was heated in a Pyrex glass tube at 255–260°C. for one hour under vacuum. The apparatus and procedure have been previously described (9). The per cent weight loss of the polymer varied from 6 to 15%; purification by continuous extraction with benzene increased its thermal stability.

Lal's polymer, synthesized from bis(chloromethyl) sulfide and sodium sulfide monohydrate decomposed at 190°C. to give s-trithiane (1). Trithiane formation is based on sulfonium salt formation (10) initiated by the presence of chloromethyl end-groups in the polymer. Wohl's polymer (2) and our own not containing these end-groups gave different decomposition products. We isolated and identified only carbon disulfide, dimethyl sulfide, and trace amounts of benzene. Work on further stabilizing this polymer to prevent end-group unzippering is in progress.

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CONCERNING THE DIETHYLENETRIAMINE-CELLULOSE COMPLEX

In a previous publication Segal and Loeb (1) concluded that in the diethylenetriamine-cellulose complex two cellulose chains are cross-linked through the secondary and one primary amino group of the triamine molecule. This was based on (a) the close similarities of the x-ray diffractograms of the diethylenetriamine- and the ethylenediamine-cellulose complexes, (b) the belief that the identical values of the 101 interplanar spacings indicated chain separation by a triamine moiety equal in length to the ethylenediamine molecule, and (c) the thought that the distance between the primary and the secondary amino groups in the extended triamine molecule is equal to that between the amino groups of the extended ethylenediamine molecule. However, it now appears that this conclusion should be revised because of some further experiments and considerations.

Until recently diffractograms from only dry complexes had been obtained by the author, but a special specimen holder designed for handling amine-wet samples (2) has now permitted an extension of the earlier studies. Diffractograms of triamine-wet complexes of celluloses I and II (Figs. 1B and 2B) were startling in that they differed markedly from that previously obtained for the dry cellulose I complex, (36.7% triamine) (Fig. 1E). Partial removal of the triamine from the triamine-wet sample, by evaporation under reduced pressure, gave dry fibers (45-46% triamine) whose diffractograms (Figs. 1C and 2C) were still very similar to those of the triamine-wet complexes! After further evaporation, to 20-23% triamine, the diffractograms (Figs. 1D and 2D) then more nearly agreed with the earlier one for the complex, Figure 1E. This is the first instance encountered where the diffractograms of dry complexes and their amine-wet counterparts have differed so. The small difference in 101 interplanar spacing for diamine-wet materials and dry complexes noted and commented on in an earlier paper (3) are now attributed to the different experimental conditions and methods used with the samples. No such difference was found when the wet and dry samples were handled identically (2). Also unusual in the present work is the retention by the dry material of the "wet complex" structure which later shifted to the "dry" structure.

The diffractograms of the triamine-wet samples indicate crystalline parameters more nearly of the order of those found in the hexamethylenediamine-cellulose complex (2, 3). This similarity, not realized earlier, can be expected because of the nearly equal chain lengths of the two amines in the extended state, with bonding occurring through the terminal primary amino groups. This bonding could still prevail in the dry tri-

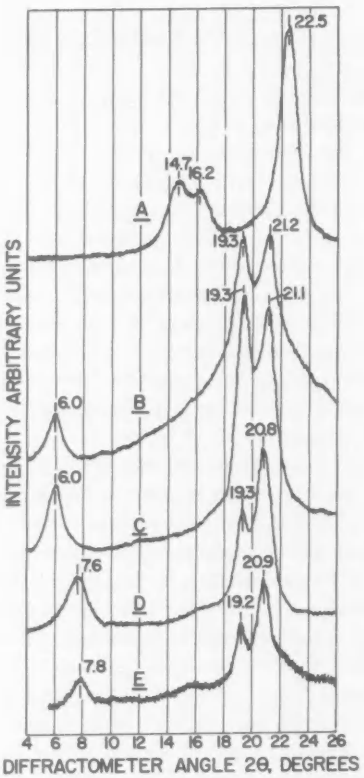

Fig. 1. X-ray diffractograms of cellulose I and the cellulose I – diethylenetriamine complexes. (A) Untreated cellulose I; (B) triamine-wet sample; (C) dry yarn, 46% triamine; (D) dry yarn, 23% triamine; (E) earlier complex of Segal and Loeb, 36.7% triamine.

amine complex where interplanar distances of a lesser magnitude are indicated, if consideration is given to possible forms that the triamine molecule can assume. While hexamethylenediamine is theoretically capable of several forms, it is definitely found in the extended state in the solid crystal (4). On the other hand, diethylenetriamine in monomeric coordination compounds with metal ions has to assume a folded shape. A molecular model of the triamine shows at least three symmetrical folded shapes where the distance between the terminal primary amino groups is equal to that of the extended ethylenediamine molecule. It is conceivable that with removal of triamine past a certain point, collapse of

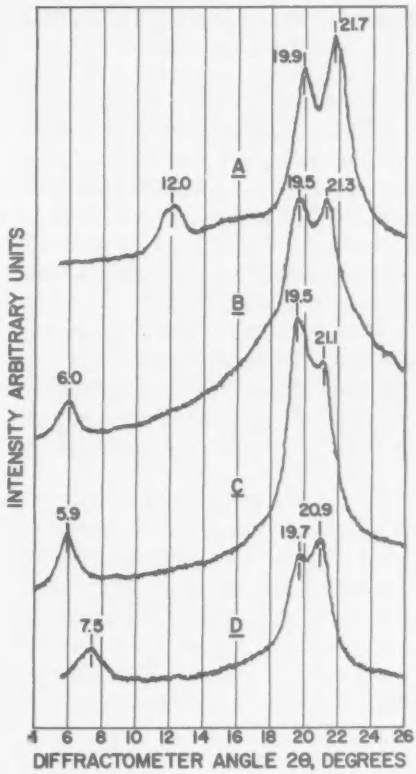

Fig. 2. X-ray diffractograms of cellulose II and the cellulose II – diethylenetriamine complexes. (A) Untreated cellulose II; (B) triamine-wet sample; (C) dry yarn, 45% triamine; (D) dry yarn, 21% triamine.

the swollen cellulose gross structure could force the extended triamine molecule into one of these folded shapes, resulting in a crystalline structure still bonded through terminal primary amine groups and with parameters still similar to those of the ethylenediamine-cellulose complex.

Information on complexes of cellulose with secondary amines seems to be lacking in the literature, and therefore there has been little basis until now for questioning that part of the earlier conclusion of Segal and Loeb relating to such bonding in the triamine-cellulose complex. However, the diffractograms of celluloses I and II wet with 1,4,7-trimethyldiethylenetriamine, with N,N′-dimethylethylenediamine, and with diethylamine, all secondary amino analogs of proven cellulose complexing agents, were obtained, and all failed to show any changes in crystal

lattice of the celluloses. When cellulose was swollen with liquid ammonia prior to introducing the above amines, in a manner similar to that described by Davis and co-workers (5) for monoethanolamine, diffractograms were obtained showing evidence of a disordered lattice, these being similar for each of the samples. This suggested not definite coordination compounds, but a sort of "occlusion cellulose" effect in the crystalline region, a trapping of the amines when the ammonia was removed. These experiments with the secondary amines, then, would seem to add further evidence for a triamine-cellulose structure bonded through the terminal amino groups of the triamine, and not through the secondary and one primary amino groups as first concluded. Bonded in the former manner above, then the triamine molecule crosslinking two cellulose chains would be extended to full length in the triamine-wet samples as well as those of more than 45% triamine content; it would assume a folded shape in complexes of less than 38% triamine where the diffractogram resembles that of the ethylenediamine-cellulose complex.

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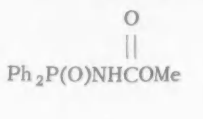
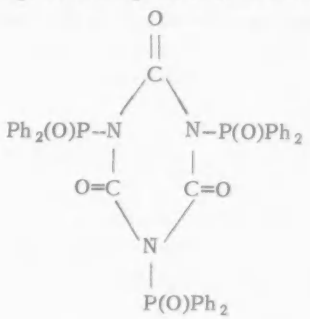
DIPHENYLPHOSPHINIC ISOCYANATE AND ITS HOMOPOLYMERIZATION

Diphenylphosphinic isocyanate, $Ph_2P(O)NCO$, was prepared for use as an intermediate in one phase of our research on phosphorus-containing polymers. A literature search revealed that it was not known; however, monoisocyanates of the general structure $(RO)_2P(O)NCO$ were reported by Kirsanov et al. (1), and Haven (2). We applied Haven's method for the preparation of $Ph_2P(O)NCO$, i.e., we reacted diphenylphosphinic chloride with silver cyanate in dry acetonitrile. The product was isolated by vacuum distillation of the AgCl-free filtrate of the reaction mixture. It had a boiling point of 163–165°C. at 0.15 mm., a melting point of 50–55°C. and contained 63.50%, C; 4.04%, H; 5.65%, N; 12.68%, P. (ANAL. Calcd. for $Ph_2P(O)NCO$: C, 64.20%; H, 4.15%; N, 5.76%; P, 12.73%); its molecular weight was 246 (theory: 243). The infrared spectrum of the compound showed absorptions for P ⟶ O, P–Ph, and NCO. We established that its structure is $Ph_2P(O)NCO$ rather than $Ph_2P(O)OCN$ by the isolation of its reaction products with H_2O and MeOH; these products were diphenylphosphinic amide, $Ph_2P(O)NH_2$, and methyl N-(diphenylphosphinyl)carbamate (I), respectively. The latter had a melting point of 97–102°C., a molecular weight of 280 and contained 61.58%, C; 5.14%, H; 5.44%, N; 11.52%, P (ANAL. Calcd. for $C_{14}H_{14}NO_3P$ (I): C, 61.10%; H, 5.14%; N, 5.03%; P, 11.24%; mol. wt. 275). The amide $Ph_2P(O)NH_2$ melted at 160–163°C. (ANAL. Calcd. for $Ph_2P(O)NH_2$: C, 66.35%; H, 5.58%; N, 6.45%; P, 14.25%; Found: C, 66.33%; H, 5.20%; N, 6.16%; P, 14.86%) and did not give any melting point depression with $Ph_2P(O)NH_2$ prepared by the aminolysis of $Ph_2P(O)Cl$ (3). It is reasonable to assume that a rearrangement of cyanate to isocyanate did not take place during the reaction of the product with H_2O or MeOH



I



II

Diphenylphosphinic isocyanate was soluble in acetonitrile, benzene, chloroform, ether and N,N-dimethylformamide. White solids deposited rapidly from its dioxane, acetonitrile and especially from its ether solution. The solid isolated from an ether solution had a melting point of 144–162°C., contained 64.43%, C; 4.81%, H; 6.13%, N; 13.17%, P, and had infrared absorptions for P ⟶ O, P–*P*h, and C(O)N. The amide absorption at 5.8–5.9 μ is strong evidence that $Ph_2P(O)NCO$ homopolymerized to 2,4,5-trioxo-1,3,5-tris(diphenylphosphinyl)hexahydro-1,3,5-triazine (II). (ANAL. Calcd. for $[Ph_2P(O)NCO]_3$ (II): C, 64.20%; H, 4.15%; N, 5.76%; P, 12.73%). This can be considered as another proof that our product is an isocyanate. When the acetonitrile filtrate of our reaction mixture was not distilled immediately after completion of the reaction, varying amounts of a white solid precipitated and decreased the yield of $Ph_2P(O)NCO$ significantly; depending on the rate of heating, this solid melted in the range of 140–200°C. and its infrared spectrum was identical with that of the solid isolated from the ether solution. Thus, it is assumed that it is the trimer II. In one case we found that the solid precipitated from an acetonitrile solution had a molecular weight of 789 (Calcd. for $(C_{13}H_{10}NO_2P)_3$ (II): mol. wt. 729) and its elemental analysis was in agreement with the values calculated for II.

This work was supported in part by the Office of Naval Research. The cooperation of Pennsalt's Analytical Department, the interpretation of the infrared spectra by Miss Ruth Kossatz and the assistance of Miss B. D'Iorio in the experimental work are gratefully acknowledged.

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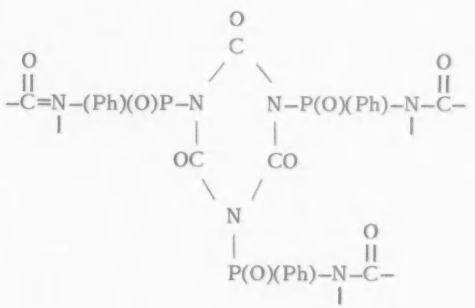
PHENYLPHOSPHONIC DIISOCYANATE AND SOME OF ITS REACTION PRODUCTS AND COPOLYMERS

A number of alkylphosphonic diisocyanates, benzylphosphonic diisocyanates, and phenylphosphonous diisocyanates have been prepared by the reaction of the appropriate dichlorides with silver cyanate, and identified (1,2). These compounds were purified by distillation; however, when an attempt was made to isolate phenylphosphonic diisocyanate (I) it polymerized (1). This last product was of interest for our studies of phosphorus-containing polymers. It was necessary, however, to isolate pure I to minimize or avoid contamination with homopolymeric $PhP(O)(NCO)_2$, and to be able to study the properties of $PhP(O)(NCO)_2$.

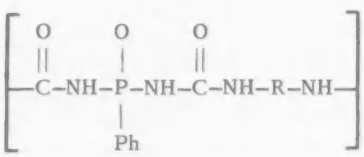
We applied the preparative method described by Haven (1) and previously used by Forbes and Anderson (3,4) for the syntheses of $P(NCO)_3$ and $P(O)(NCO)_3$. The conversion was 100% on the basis of the silver chloride isolated. The filtrate of the reaction mixture formed a white solid on standing and then yielded only small amounts of product; however, when the AgCl-free filtrate was distilled immediately after the reaction was completed, the yields were comparatively good and in one case exceeded 70%.

$PhP(O)(NCO)_2$ $PhP(O)[NHC(O)NHPh]_2$

I II



III



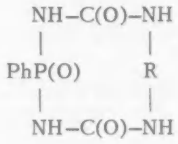
IV, R = p-C_6H_4-

IVa, R = m-C_6H_4-

$PhP(O)[NHC(O)NHRNH_2]_2$

V, R = p–C_6H_4–

Va, R = m–C_6H_4–



VI, R = p–C_6H_4–

VIa, R = m–C_6H_4–

Pure, freshly distilled phenylphosphonic diisocyanate is a colorless oil boiling at 113–114°C. at 0.75 mm. Its structure was confirmed by its elemental analysis, infrared spectrum and reaction product with aniline, i.e., phenylphosphinylidene-bis (3-phenylurea) (II). It became yellow on standing but did not form any solids even after a 7-month storage at room temperature; however, the infrared spectrum of the aged sample indicated some homopolymerization as evidenced by a comparatively weak absorption at 5.8–5.9 μ, characteristic for III.

The thermal stability of I was studied briefly in the hope that the data obtained would be helpful in the choice of conditions for reactions with I. It began to lose some weight at 130°C.; at up to 180°C. the loss was slow but became very rapid at 200°C. When the pyrolysis temperature reached 250°C. at the rate of 5°C./min., the weight loss was 28%, increased by 3–4% after 1 hr. at 250°C., and did not change any more during an additional 2 hr. at 250°C. At least 35.7% of the total 31.7% weight loss was CO_2. The pyrolysis residue was a brittle yellowish solid of the composition $C_{7.2}H_{6.2}N_{1.9}O_{1.7}P$ and its infrared spectrum did not show any absorption peaks at 4.4 μ characteristic for NCO-groups. Since there was considerable solidification during the heating at 130–180°C. it can be assumed that I rearranged or homopolymerized before a significant weight loss occurred. This pyrolysis study was helpful in the interpretation of the product obtained by the addition copolymerization of I with p-phenylenediamine.

Phenylphosphonic diisocyanate reacted somewhat exothermically with p-phenylenediamine in acetone solution. The product isolated was insoluble in acetone and melted at 188–190°C. with some decomposition; on the basis of the elemental analysis it had a composition of $C_{11.6}H_{14.4}N_{3.0}O_{2.8}P$. Its infrared spectrum showed the absence of NCO-groups and was similar to that of II in the region of 5.9–6.5 μ with additional –C(O)N= absorption at 5.8–5.9 μ. As noted above, the aged sample of $Ph(O)P(NCO)_2$ also absorbed at 5.8–5.9 μ and we assume that this absorption is due to a cyclic homopolymerization (most probably structure III). The elemental analysis and the infrared spectrum of the product suggested that it is a mixture of 70% of copolymer IV with 30% of III. This assumption was also supported by the behavior of the prod-

uct at elevated temperature: its weight loss of 9.4% at 250°C. was in full agreement with the presence of 30% of homopolymeric I, i.e., III, which lost 31.7% at 250°C. The possibility that this product mixture might contain phenylphosphinylidene-bis(3-p-aminophenylurea) (V) or 1, 1′-phenylphosphinylidene-3, 3′-p-phenylenediurea (VI) is not excluded.

The reaction of I with m-phenylenediamine resulted in a product melting at 185–190°C. Its infrared spectrum and elemental analysis suggested that it was a mixture of 80% of IVa (or Va and VIa) and 20% of homopolymer III.

Experimental

Preparation of Phenylphosphonic Diisocyanate (I)

A mixture of 105.0 g. (0.7 mole) silver cyanate in 500 cc. acetonitrile freshly distilled over P_2O_5 was vigorously stirred at about 20°C. in a four-neck, two-liter round bottom flask equipped with an addition funnel, stirrer, reflux condenser, and thermowell. A drying tube charged with calcium chloride was attached to the outlet of the reflux condenser. Phenylphosphonic dichloride, 64.5 g. (0.33 mole), was added slowly to the reaction mixture at a rate such that the reaction temperature remained at 20–30°C. The reaction mixture was refluxed (82–84°C.) for 1.5 hr. and filtered at 20–25°C.; the filter cake was washed with acetonitrile and the combined filtrates were distilled. After removing the solvent, 15.7 g. (22.8%) of phenylphosphonic diisocyanate was obtained having a boiling point of 113–114°C. at 0.75 mm. It is a colorless liquid, soluble in aromatic and aliphatic hydrocarbons, chlorinated hydracarbons, acetonitrile, ethers, dioxane, tertiary amines, N,N-dimethylformamide, and reacts with water, alcohols, and primary and secondary amines. Its infrared spectrum shows absorptions characteristic for C_6H_5–P, P–O and –N=C=O and absence of any absorption characteristic for the carbonylamide group. A sample stored for seven months became yellow and its infrared spectrum showed a very weak absorption for carbonylamide group at 5.8–5.9 μ indicative of homopolymerization.

ANAL. Calcd. for $C_8H_5N_2O_3P$(I): C, 46.20%; H, 2.40%; N, 13.30%; P, 14.90%. Found: C, 46.30%; H, 2.56%; N, 13.40%; P, 14.94%.

The dry filter cake, 108.0 g., contained 21.8% Cl representing a 100% conversion of the phenylphosphonic dichloride to silver chloride.

The yield of phenylphosphonic diisocyanate could be increased to 74% by a fast distillation of the AgCl-free reaction mixture at lower temperature and lower pressure.

The AgCl-free reaction mixture deposited a white solid when stored for 24 hr.

Pyrolysis of Phenylphosphonic Diisocyanate (I)

A pyrolysis was carried out in a quartz-spiral spring thermal balance of a design similar to the equipment described by Gordon and Campbell (5).

A sample of 2.7786 g. of phenylphosphonic diisocyanate in a 13–cc. platinum crucible was pyrolyzed for 2.5 hr. at 250°C. under nitrogen atmosphere. The temperature was raised to 250°C. at a rate of 5°C. per minute. The weight of the pyrolysis residue, 1.8925 g. (68.3%), remained constant during the last two hours at 250°C. At least 0.313 g. (11.3% of 2.7786 g. charged) of the volatile material was CO_2. The yellow brittle solid pyrolysis residue softened at about 225°C. and did not melt at up to 285°C.

Found: C, 48.21%; H, 3.50%; N, 15.48%; P, 17.38%. Empirical composition: $C_{7.2}H_{6.2}N_{1.9}O_{1.7}P$.

Reaction of Phenylphosphonic Diisocyanate (I) with Aniline. Phenylphosphinylidene-bis(3-phenylurea) (II).

A solution of 1.0 g. (0.005 mole) phenylphosphonic diisocyanate in 20 cc. ether was added slowly to a solution of 5.1 g. (0.055 mole) aniline in 20 cc. ether; an exothermic reaction took place and a solid precipitated. It was filtered to obtain 1.88 g. (93%) of phenylphosphinylidene-bis(3-phenylurea) (II) having a melting point of 193–195°C. The infrared spectrum of the compound showed the presence of amide, P → O, and P–C_6H_5, and is in agreement with the structure II.

ANAL. Calcd. $C_{20}H_{19}N_4O_3P$ (II): C, 60.90%; H, 4.83%; N, 14.20%; P, 7.87%; Found: C, 60.82%; H, 4.97%; N, 14.11%; P, 7.71%.

Reaction of Phenylphosphonic Diisocyanate (I) with p-Phenylenediamine

A solution of 1.0 g. (0.01 mole) p-phenylenediamine in 15 cc. dry acetone was added dropwise to a stirred solution of 2.0 g. (0.01 mole) phenylphosphonic diisocyanate in 20 cc. dry acetone. A slightly exothermic reaction took place and a gray solid was formed. The reaction mixture was refluxed for one hour and filtered at room temperature to isolate 2.9 g. of a solid melting at 188–190°C. (some decomposition).

ANAL. Calcd. for 70% of $C_{14}H_{13}N_4O_3P$ (IV) + 30% of $(C_8H_5N_2O_3P)_n$ (III): C, 51.17%; H, 3.62%; N, 15.99%; P, 11.35%. ANAL. Calcd. for $C_{14}H_{13}N_4O_3P$ (IV): C, 53.20%; H, 4.12%; N, 17.20%; P, 9.82%. Found: C, 51.10%; H, 5.30%; N, 15.42%; P, 11.36%. Empirical composition: $C_{11.6}H_{14.4}N_{3.0}O_{2.8}P$.

A sample of 0.3487 g. of this reaction product was pyrolyzed in a Chevenard thermobalance under nitrogen atmosphere. The temperature was raised at the rate of 5°C. per minute until it reached 240°C. It was held at 240–250°C. for 15 min. and at 250°C. for 1.5 hr. The pyrolysis residue, melting point 185–205°C., had a constant weight of 0.3153 g. (90.6%) for the entire time at 250°C. Its infrared spectrum showed the absence of NCO-groups, the presence of P $\longrightarrow$ O,P–Ph, p-substitution in the ring, and carbonyl amide absorptions in the region of 5.8–6.5 μ.

Found: C, 52.02%; H, 3.81%; N, 14.18%; P, 11.37%. Empirical composition: $C_{11.8}H_{10.4}N_{3.0}O_{3.2}P$.

Reaction of Phenylphosphonic Diisocyanate (I) with m-Phenylenediamine

The acetonitrile solution of equimolar amounts of phenylphosphonic diisocyanate and m-phenylenediamine were mixed under stirring. An exothermic reaction took place and a gray solid precipitated. The reaction mixture was refluxed for 5 min. and filtered at room temperature to obtain a gray solid melting at 185–190°C.

ANAL. Calcd. for 80% of $C_{14}H_{13}N_4O_3P$ (IV-a) + 20% of $(C_8H_5N_2O_3P)_n$ (III): C, 51.85%; H, 3.78%; N, 16.41%; P, 10.84%. Found: C, 52.27%; H, 4.55%; N, 16.14%; P, 10.12%. Empirical composition: $C_{13.3}H_{13.9}N_{3.5}O_{3.2}P$.

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POLYMER LETTERS VOL. 1, PP. 253-256 (1963)

CRYOSCOPIC SEGMENT WEIGHT OF POLYISOPRENE AND POLYBUTADIENE RUBBER

According to the older literature (1),with special attention to the work of Staudinger, dilute solutions of natural rubber in benzene freeze at the same temperature as the pure solvent. A recent report (2) deals with moderately low concentrations for which depressions of up to 0.7°C. were observed. However, it is known that vulcanizates (3) swollen to equilibrium in benzene may show depressions of up to about 20°C.

We now can report preliminary measurements of the freezing of solutions containing from one to about four times as much benzene as cis-1,4-polybutadiene rubber or for the single system containing 1.4 times as much benzene as natural rubber.

Figure 1 shows a typical cooling curve for a mixture of 25.00 g. freshly milled pale crepe natural rubber and 35.00 g. benzene. The mixture had stood for 12 days at 25°C. and was contained in a 35 mm. test tube. It was not stirred before or during the temperature measurements. A mercury filled thermometer graduated in 0.2°C. was used. Cooling was provided by a −15°C. bath separated from the test tube by a 1 cm. annular air space.

The depression in melting point indicated in Figure 1 to be 4.0°C. is due to benzene-soluble nonrubber constituents and polyisoprene in the sample. About 0.3°C. may be assigned to the effect of nonrubber components which leaves 3.7°C. as the depression due to polyisoprene. This temperature can be used in the freezing point depression equation derived from the Clapeyron-Clausius equation to calculate a molecular weight value for the rubber. It is assumed that the solvent vapor acts

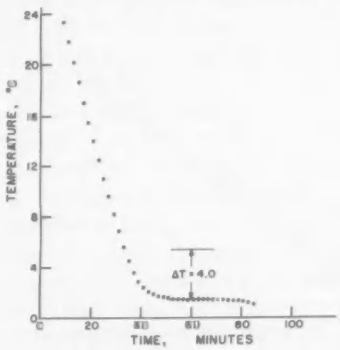

Fig. 1. Cooling curve for mixture of 25.00 g. pale crepe rubber and 35.00 g. benzene.

as an ideal gas, and that Raoult's law is obeyed, so that

$$\ln X_1 = -(L_f/R)[(1/T) - (1/T_0)]$$

where X_1 is the mole fraction of the solvent, L_f (= 2370 cal./mole) is the molar heat of fusion of the solvent, R the gas constant, T_0 the freezing point of the pure solvent, and T the freezing point of the solution. Under these conditions the molecular weight value calculated for the rubber is 909. This we call the cryoscopic segment weight, M_F.

A determination in the same way on 25.00 g. all cis-polybutadiene ($[\eta]_0$ C_6H_6, 25° = 2.45) in 35.00 g. of benzene ($\Delta T = 5.2°$) gave a value for M_F of 649. It is to be expected that the segment weight of both polyisoprene and polybutadiene will depend to a first approximation on the weight of a given length of the polymer chain. On the basis of four chain atoms this will be 68 units for polyisoprene and 54 for polybutadiene. The M_F for polyisoprene multiplied by 54/68 should then give the value which might be expected for M_F for polybutadiene. The value $909 \times 54/68 = 722$ is in reasonable agreement with the found value of 649.

Vapor pressure data for mixtures of benzene and rubber were determined by Gee and Treloar (4). From Raoult's law and their data a mixture containing 1.4 parts benzene and 1 part rubber can be calculated to have an effective molecular weight of 1,280, a value somewhat higher than M_F of 909.

M_F should depend on polymer solvent interaction and hence should vary with concentration. Figure 2 shows this to be true for varying concentrations of fractions of cis-1,4-polybutadiene. The solid circle is for

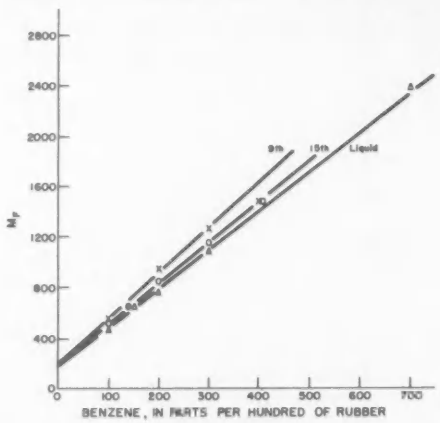

Fig. 2. Effect of volume swell on segment weight of polybutadiene in benzene.

the unfractionated polymer ($[\eta]_0 = 2.45$). The M_F values for the 15th fraction ($[\eta]_0 = 2.59$) and 9th fraction ($[\eta]_0 = 1.43$) are shown as circles and crosses, respectively. The triangles are for an alkyllithium initiated polybutadiene so low in molecular weight (ca. 10,000) that it was a liquid (5). The data in Figure 2 show these samples of polybutadiene to have similar M_F values which extrapolate at 0% solvent to M_F values of 160 to 200. At 100% benzene (on 100 of rubber) ΔT amounts to ca. 9° and at 400% to about 0.8°. The small differences, if real, in slopes of the curves in Figure 2 are possibly due to different small amounts of branches or crosslinks in the different specimens. They cannot be due to differences in primary molecular weight.

The polyisoprene and polybutadiene polymers used for the data of Figures 1 and 2 were rapidly and completely soluble in benzene. They are believed to be relatively free of covalent crosslinks. When they were vulcanized in a recipe containing sulfur 2.5, benzothiazyl disulfide 1, zinc oxide 5, and stearic acid 4, all in parts per 100 parts by weight of rubber, the M_F values showed a marked dependence on time of cure. The NR mix was cured at 284°F. and the polybutadiene at 302°F. The NR was fully cured at 60 min. and the polybutadiene at 90 min. Specimens of the polybutadiene stock cured in the form of spheres for from 120 to 240 min. and weighing about 23 g. were prepared. The 120 and 240 min. cures showed an equilibrium limiting swell of about 400% in benzene due allowance being made for curing ingredients. A thermometer well was provided in each specimen and swelling with different amounts of benzene carried out. The absorption of solvent is fairly rapid but in order for the swollen state to equilibrate it is necessary for any specimen to stand in a closed container in the absence of liquid solvent for several days or several weeks. The freezing point thermometer was inserted in the swollen sphere which then was placed in a tube and covered with a heat-conducting medium which consisted of a 50:50 mixture of glycol and water. The cooling experiment was then run as for uncured specimens. The M_F values for the 120 and 240 min. cures depended very little on the amount of benzene. At 164% benzene (on 100 of rubber) the M_F was found to be 284 and at increasing per cent swells the M_F dropped slowly until at 400% (approximately equilibrium swell) M_F = 192. This value is within the range of 160 to 200 for M_F at 0% swell for the uncured rubber. Indeed this is the result to be expected if the main function of physical crosslinks in uncured, unswollen rubber is the same as for chemical crosslinks in cured, swollen rubber.

The natural rubber stock when fully cured in the mold used for the polybutadiene cures gave an M_F value of about 246 at 164% swell in benzene. This value multiplied by 54/68 gives 196 as the calculated value for polybutadiene to be compared with the found value of 284 at 164% swell in benzene.

As evidence that the freezing point depressions obtained in this work

without stirring have meaning for cryoscopic purposes, toluene was tested as a solute in place of rubber. A mixture of 5.00 g. toluene and 50.00 g. benzene was found to give a ΔT of 5.5°. These numbers inserted in the freezing point equation give a found molecular weight of 90.9 as compared to the calculated value of 92.

The cryoscopic segment weight is thus seen to be easily ascertained from measurements made on concentrated polymer solutions for soluble polymers or on swollen networks in the case of crosslinked polymers. We believe that this segment weight is fundamental, not only to solution behavior, but also for describing the response of the polymers to any deforming force. It is related to the Eyring theory (6) flow unit, i.e., for a butadiene rubber, to about 25 carbon chain atoms consisting of some 325 molecular weight units. The "behavior units," larger than the cryoscopic segment and which may be used to describe the response to a given deformation, must then include assemblages of a number of cooperative elementary cryoscopic segments. We have found for polybutadiene of sufficient primary molecular weight to display segmental cryoscopic action that the segment weight according to Figure 2 is about 200 molecular weight units.

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POLYMER FRACTIONATION STUDIES IN THE SOLID STATE POLYMERIZATION OF ACRYLAMIDE*

It has been known for some time that acrylamide can be polymerized in the crystalline state by exposure to ionizing radiation. Detailed kinetic studies were published on both the "in-source" and "post-irradiation" reaction (1-4). The usual homogeneous phase kinetic concepts are not readily applicable and the reaction has generally been analyzed from a solid state chemistry viewpoint (1-4). Though the reaction is presumed to be free radical in character, the usual steady state assumption for radical concentration was found to be inadequate because there seemed to be no normal free radical termination step. The present authors have previously presented kinetic data, as well as evidence from x-ray diffraction, electron spin resonance, and optical microscopy, which are mutually consistent with a proposed mechanistic picture. The solid state polymerization was pictured as proceeding by a nucleation mechanism in which free radicals initiate reaction at defects, propagate at a monomer-polymer interface and are eventually trapped by overlapping of reactive sites (2). Recent electron microscopy studies (5) also supported the heterogeneous feature of acrylamide polymerization.

It was claimed, however, that the number of chains would be constant throughout the post irradiation reaction and that consequently the initial free radical concentration could be calculated from the yield and molecular weight data (3). It would be difficult to reconcile such a picture with the proposed nucleation mechanism. Consequently, fractionation studies were made on polymer from both "in-source" and "post-irradiation" experiments with the hope that the resultant data might further clarify the issue.

Experimental

The acrylamide used was an American Cyanamid product. It was recrystallized three times from acetone, dried thoroughly in vacuum and had a melting point of 84°C.

Appropriate amounts of acrylamide were measured into Pyrex tubes which were evacuated overnight at 10^{-4} mm. The tubes were sealed, weighed, and irradiations performed in the Brookhaven National Laboratory Co-60 radiation facility (6). Dosimetry measurements were performed using the Fricke dosimeter method (7).

Polymer from the "in-source" experiment was obtained by irradiating

*This work was performed under the auspices of the U.S. Atomic Energy Commission.

TABLE I

Fractionation Data for Post Irradiation Acrylamide Polymer

Fraction No.	Wt.–% of fractions	No. of moles–% of fractions	(η)	M_n
BB–A	8.09	4.39	2.70	286,000
BB–B	13.21	7.97	2.64	257,000
BB–C	9.83	7.12	1.97	214,000
BB–D	11.68	8.47	1.94	214,000
BB–E	4.29	3.13	1.96	212,000
BB–F	16.40	12.05	2.00	211,000
BB–G	10.04	9.11	1.41	171,000
BB–H	13.52	17.48	1.20	130,000
BB–I	7.50	13.80	0.71	84,300
BB–J	5.46	16.47	0.46	51,400

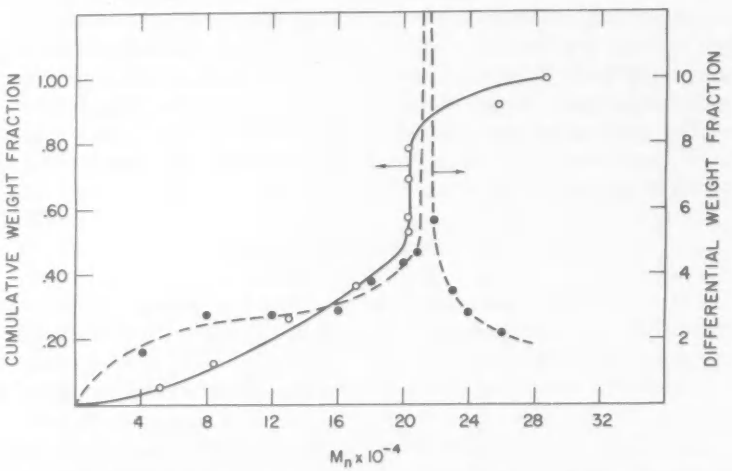

Fig. 1. Cumulative and differential weight distribution for post irradiation acrylamide polymer. Irradiation dose 0.8 Mrad. at –78°C. Post irradiation storage, 360 hr. at 25°C. Conversion 18.34%. (○) Cumulative, (●) differential molecular weight distribution.

TABLE II

Fractionation Data for In-Source Acrylamide Polymer

Fraction No.	Wt.–% of fractions	(η)	M_n	Branch points per molecule
AG–1	12.25	2.27	643,000	17
AG–2	8.65	1.85	468,000	12
AG–3	11.64	1.57	367,000	9
AG–4	9.64	1.20	214,000	7
AG–5	9.29	1.09	198,000	6
AG–6	9.96	0.90	161,000	5
AG–7	10.07	0.71	101,000	3
AG–8	6.79	0.55	67,700	–
AG–9	9.79	0.41	42,900	–
AG–10	6.90	0.21	15,000	–
AG–11	5.06	0.090	9,000	–

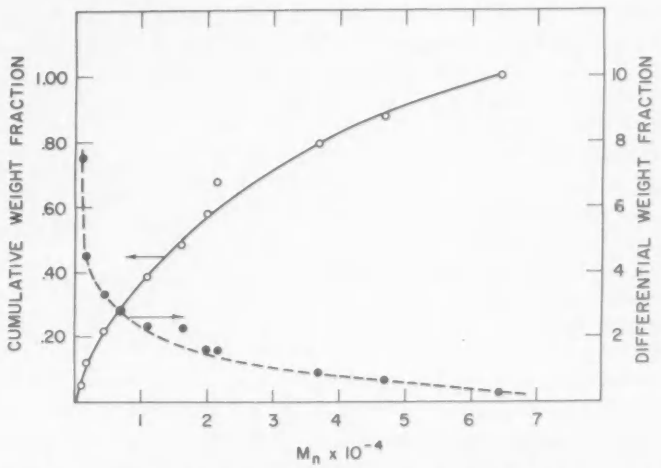

Fig. 2. Cumulative and differential weight distribution for in-source acrylamide polymer. Irradiation dose 2.46 Mrad. at 27°C. Conversion 95%. (○) Cumulative, (●) differential molecular weight distribution.

at 27°C. to a dose of 2.46 Mrad. at a dose rate of 0.41 Mrad./hr. The sample tubes were opened immediately after irradiation and the contents poured quickly into methanol. The mixture was stirred overnight and the precipitated polymer collected on a filter funnel and dried in a vacuum oven at room temperature to constant weight. The degree of conversion was 95%.

The "post-irradiation" polymer was prepared by irradiating the monomer at −78°C. to a dose of 0.80 Mrad. at a dose rate of 0.257 Mrad./hr. and, immediately after irradiation, placing the sample tube in a constant temperature bath at 25.0°C. It was stored at this temperature for 360 hr. after which time polymer was isolated in the manner described above. The conversion to polymer was 18.34%.

The polymer was dissolved in water to produce a 0.5M solution and fractionation was effected at 30.0°C. by addition of aliquots of methanol.

Osmotic pressure determinations on the fractions were made at 25.0°C. in aqueous solutions using Stabin type osmometers and gel-cellophane membranes.

Intrinsic viscosities were also measured in water solutions at 25.0°C.

Results and Discussion

The fractionation of the "post-irradiation" polymer, 6.00 g., yielded 10 fractions with a recovery of 97.3%. These results are given in Table I. It is interesting to note that four fractions, BB–C to BB–F, representing 42 wt.–% of the polymer, have essentially the same intrinsic viscosity and number average molecular weight. These data give a peculiar cumulative and differential weight distribution curve shown in Figure 1.

Fractionation of the "in-source" polymer, 8.00 g., yielded 11 fractions with a recovery of 89.9%. These data, given in Table II, show a very broad molecular weight distribution. The cumulative and differential weight distribution curves are plotted in Figure 2.

Finally, using the data in Tables I and II plots of log M_n versus log (η) were constructed and these appear in Figure 3. The following relationships can then be established: (a) "post-irradiation" polymer

$$(\eta) = 4.07 \times 10^{-6} M_n^{1.07}$$

and (b) "in-source" polymer

$$(\eta) = 4.65 \times 10^{-4} M_n^{0.64}$$

The broad molecular weight distribution from the "in-source" polymer is not too difficult to explain. The growing chains have very long life-

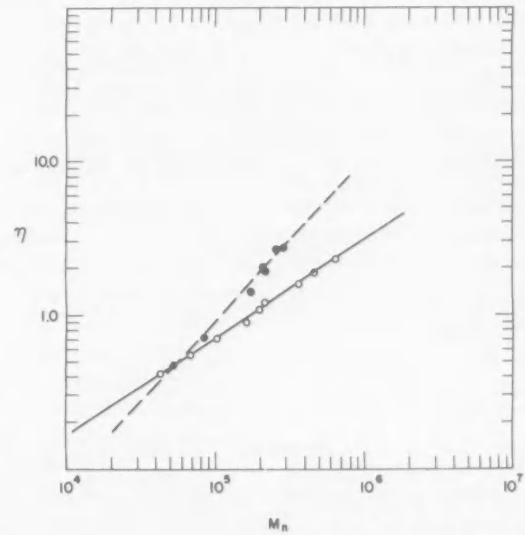

Fig. 3. Intrinsic viscosity – molecular weight relationship for polyacrylamide. (——) in-source polymer, (– –) for post-irradiation polymer.

times so there is a continuously increasing number of polymerizing species. Also, since the polymer as formed is exposed to radiation, it too becomes affected. Free radicals can then be generated on the polymer chains leading to branching. This is borne out by the relatively low intrinsic viscosities obtained. The number of chain branches can be calculated by the Stockmayer and Fixman (8) method comparing the intrinsic viscosity of branched and linear polymer chains. The results of such a calculation are included in the last column of Table II.

The occurrence of a significantly large percentage of polymer of constant molecular weight from the "post-irradiation" experiment is more interesting but also more difficult to explain. A number of alternative suggestions may be offered. (1) The size to which any polymer chain grows is limited by the critical size of the crystal region in which the reaction is occurring. (2) All chains begin initiating polymerization simultaneously as Morawetz (4) has suggested. Some variation in molecular weight must be expected because propagation rates can be expected to differ in different crystal environment. (3) Radicals begin initiating polymerization at different times depending on the crystal environment in which they are formed and trapped.

Obviously in each of these cases one can account for the large fraction of constant molecular weight polymer by specifying that the chains lead-

ing to this species are initiated or propagated at types of defects or crystal regions which are most prevalent. It is impossible to clearly differentiate the most probable alternative with the data presently available.

Further fractionation data will be obtained as a function of polymer yield and for polymers made from monomers crystallized under vastly different preparative techniques. A more complete discussion of this subject will then be possible.

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THE POLYMERIZATION OF N-VINYLCARBAZOLE IN THE PRESENCE OF CARBONTETRACHLORIDE

In our experiments on the polymerization initiated by electrolytically discharged ions it was found that N-vinylcarbazole underwent a cationic polymerization initiated by the discharge products of perchlorate and borofluorate ions (1). This effect was thought to be the result of the nucleophilic reactivity of the nitrogen atom in N-vinylcarbazole. Therefore, it was very interesting for us to learn that Chapiro and Hardy (2) observed a spontaneous polymerization in a system consisting only of N-vinylcarbazole and carbon tetrachloride without any initiator. These authors ascribed the initiation to free radicals formed from a N-vinylcarbazole carbon tetrachloride complex but from our point of view a ionic mechanism seemed more probable.

To decide this question we carried out some copolymerization experiments in this system. As a second monomer, methyl methacrylate was chosen. In a system consisting of 0.70 g. methyl methacrylate, 1.85 g. N-vinylcarbazole, and 0.80 g. carbon tetrachloride after 16 hr. at 30°C. 0.48 g. polymer were obtained. Elemental analysis showed this polymer to be nearly pure poly-N-vinylcarbazole (theor.: 7.25% N, found: 7.22% N) whereas in the case of a free radical mechanism a copolymer with $\sim$ 2.5% N should have been formed (3).

Similar results have been obtained with other feed compositions. In the system N-vinylcarbazole methyl methacrylate polymerization was also initiated by sulfuric acid (e.g., 1.11 g. N-vinylcarbazole, 0.94 g. methyl methacrylate, 1 ml. 1% H_2SO_4 in i-amyl ether) and yielded pure poly-N-vinylcarbazole. Therefore, also in the carbon tetrachloride system a cationic polymerization of N-vinylcarbazole takes place. A nucleophilic attack on the carbon atom of carbon tetrachloride is possibly the initiating step. In the carbon tetrachloride system a yellow to orange color is developed during the reaction, as already observed by Chapiro and Hardy, whereas with sulfuric acid the system remains colorless.

The authors wish to acknowledge with gratitude partial support of this study by Continental Oil Company Ponca City, Oklahoma.

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DIELECTRIC PROPERTIES OF POLYMETHACRYLIC ESTERS IN DILUTE SOLUTIONS

Since for simple polar molecules the dipole moment may give information about the molecular structure and conformation, it has been thought useful to measure the dipole moment of polar macromolecules in solution. Investigations in this field were done by Debye and Bueche (1), de Brouckère and coworkers (2), Marchal (3), and still others. In most cases it was shown that at room temperature the mean square dipole moment (MSM) of polar polymers depends linearly on the molecular weight. In the same solutions the mean square end-to-end distance (MSD) is generally dependent on a power of M larger than unity because of so called "long range interactions." Marchal and Benoit (3) therefore concluded that the MSM should be independent of these interactions even in non-θ solvents and justified this conclusion using a very crude and non-convincing model. They predicted that due to the absence of the influence of long range interactions MSM should be nearly independent of temperature in a not too large interval. However, this last prediction has not been verified in more recent experiments by Salovey (4) who found a definite temperature variation of MSM for polymethylmethacrylate in benzene and toluene between 20 and 90°C.

In order to trace the origin of this contradictory behavior it is useful to look closely at the way in which MSM is experimentally determined. The conventional method is to assume that the polymer solute has roughly a spherical symmetry and to apply equations for $\overline{\mu^2}$ derived from Debye's theory of diluted solutions, or equivalent equations as they appear in Onsager's and Fröhlich's theory. In the former case the equation may be written:

$$\overline{\mu^2} = [2700\ kTM/4\pi N_0 d_s (\epsilon_s + 2)^2] [(\partial\epsilon/\partial x)_0 - (\partial\epsilon_\infty/\partial x)_0] \quad (1)$$

where M stands for the molecular weight of the polymer, N_0 for Avogadro's number, d_s and ϵ_s for the density and dielectric constant of the pure solvent. The terms appearing between the brackets $(\partial\epsilon/\partial x)_0 = \lim_{x\to 0} (\partial\epsilon/\partial x)$ is the slope of the curve $\epsilon = \epsilon(x)$ (where x is the mass fraction of the solute) at the origin and $(\partial\epsilon_\infty/\partial x)_0$ is the corresponding value of the dielectric constant of the solution at frequencies high enough to make contributions of orientational polarization disappear. No large error is made if ϵ_∞ is replaced by n_∞^2, the square of the refractive index extrapolated to infinite wavelength. Some authors even drop, in a first approximation the $(\partial\epsilon_\infty/\partial x)_0$ term altogether arguing that it is small compared to $(\partial\epsilon/\partial x)_0$.

The same formula (1) is also valid, in the limit of infinitely diluted solutions, for Fröhlich's theory. The Onsager formula differs from (1) through the factor before the brackets. However if the $n_\infty^2 = \epsilon_\infty$ value of the pure polymer (which is not exactly known in the liquid state) may be thought not to differ markedly from ϵ_s, Onsager's expression reduces to eq. (1). It is most important to realize that the calculated value of $(\overline{\mu^2}/M)$ will depend on the actual properties of the dilute polymer solutions only through the term between brackets in the right-hand side of eq. (1).

Very accurate dielectric measurements (5) were performed with solutions of three different polymethacrylic esters, of which three samples with different mean molecular weights were selected:

methyl:	80,000 – 380,000 – 730,000
ethyl:	190,000 – 340,000 – 700,000
n-butyl:	60,000 – 110,000 – 250,000

The following nonpolar or slightly polar solvents were used: benzene, 1,4-dioxane, CCl_4 (not for the methylesters), and toluene. It was verified that at the frequencies of the measurements no dispersion occured (the dielectric losses of the solutions were insignificantly different from those of the pure solvents). The temperature was varied between 50 and – 30°C., the lower limit depending on the t_f, of the solvent.

It was found that both ϵ and n^2 varied linearly with x so $(\partial\epsilon/\partial x)_0$ and $(\partial n_\infty^2/\partial x)_0$ are equal to the slope a and b of the straight line $|\epsilon - \epsilon_s = ax|$ and $n_\infty^2 - (n_\infty^2)_s = bx$. For a given polymer, a and b varied with the solvent but were molecular weight independent. Furthermore a did not change with temperature. For six out of eleven systems a slight decrease of b with increasing temperature was found. However, in view of the inaccurateness of b (due to successive extrapolation to infinite wavelength and to temperatures below 5°C.) and the fact that b is in all cases a factor 10 to 100 smaller than a, it may be stated that within the accuracy of the experiments (a – b) was practically temperature independent.

Application of (1) to compute $\overline{\mu^2}$, would lead to the conclusions (a) that $\overline{\mu^2}$ varies linearly with M, and (b) that $\overline{\mu^2}$ practically increases with temperature as $T/d_s(\epsilon_s + 2)^2$. This last conclusion raises the question whether eq. (1) may be used to compute $\overline{\mu^2}$ for macromolecular solutes. It is in fact difficult to understand why the MSM variation with temperature should be so closely related to the physical properties of the solvent and not to the actual properties of the polymeric molecule or its solution. Therefore, in our view, the evidence for the linear dependency of MSM on M is not well established and theoretical interpretation of experimental values for $\overline{\mu^2}$ values of polymers remain doubtful.

On the other hand it is not as difficult to understand why eq. (1), derived for homogeneous solutions, might not be applicable to dilute poly-

mer solutions. Flory (6) has stressed the fact that these solutions present a definitely inhomogeneous character. The experimental dielectric increment $\Delta\epsilon = (\epsilon - \epsilon_s)$ should therefore be interpreted rather in terms of the properties of a homogeneous suspension. The $\Delta\epsilon$ will depend on the dielectric constant of the macromolecular regions, which are large compared to the dimensions of the solvent molecules and may be considered as very concentrated solutions of highly interacting polymer segments. From this point of view it is easily understood why $\Delta\epsilon$ will not be molecular weight dependent (as long as M is sufficiently large) and not present a pronounced temperature variation.

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POLYMER LETTERS VOL. 1, PP. 269-270 (1963)

CONDUCTOMETRIC TITRATION OF CARBOXYL ENDGROUPS IN POLYAMIDES, OLIGOAMIDES AND PEPTIDES

The titration of carboxyl endgroups for molecular weight estimation of polyamides may be conducted according to the method of Waltz and Taylor (1) in benzyl alcohol at 175°C. determining the end-point conductometrically. On account of the susceptibility to oxidation of benzyl alcohol it is necessary to carry out a blank determination of the acid products produced on heating. The blank values according to Waltz and Taylor amount to 5-20 micro-equivalents per 100 ml. per hour of heating and therefore correspond roughly to the carboxyl content of 0.5 g. of commercial polymers. Since the reproducibility of these blank values is not always good, it is clear that errors may arise from this source. In addition one must bear in mind the possibilities of interaction of the oxidation products (e.g., aldehydes) with the polymer and also of esterification of carboxyl groups after long periods in solution.

Since trifluoroethanol is an excellent and easily purified solvent for polyamides and polypeptides (2), we have carried out titration in this solvent of commercial nylon 66, N-carbobenzoxy-oligo-ϵ-aminocaproic acids (3), and water insoluble peptide derivatives (e.g., N-carbobenzoxy-L-phenylalanine-L-tyrosine (4). We have used concentrations of 0.1-1 % at room temperature. The conductometric measurements were carried out with a pair of immersed platinum-foil electrodes and a measuring bridge. One may titrate with aqueous solutions of the base since the water content of the solution scarcely influences the titration and at room temperature nylon 66 is not precipitated by up to 5% water content. Particularly in the case of oligomers, which have a relatively high endgroup content, it is necessary to dry the samples carefully since higher members may absorb considerable amounts of water (5).

Example 1: 26.1 mg. (= 24.7 μmole) Z $[Cap]_8$ OH was dissolved in 50 ml. of redistilled trifluoroethanol and titrated with efficient stirring with 0.02N aqueous NaOH. Titer 1.25 ml. (calc. 1.24).

Example 2: 500 mg. of nylon 66 was dissolved in 50 ml. of trifluoroethanol with stirring and warming to 35°C. The solution was then cooled to room temperature and titrated with 0.02N aqueous NaOH. Titer 1.44 ml. corresponding to 57.6 micro-equivalents per gram.

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ERRATUM

THE MEASUREMENT OF DIFFUSION CONSTANTS OF GASES IN POLYMERS BY SORPTION TECHNIQUES

(J. Polymer Sci., B1, 19-23, 1963)

By A. S. MICHAELS, W. R. VIETH, and H. J. BIXLER, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts

On page 20, the line directly under eq.(2) should read: "For very short times, $\bar{E}$, which equals $(p_i - p)/(p_i - p_f)$, is linearly related to the square root of the dimensionless group Dt/L^2, as shown by Crank (8)." Equation (3) should read:

$$1 - \bar{E} = \frac{p - p_f}{p_i - p_f} = \frac{2\psi(1 + \psi)}{1 + \psi + \psi^2 q_1^2} \exp\{-4Dq_1^2 t/L^2\}$$

On page 21 eq. (5) should read:

$$D = \frac{L^2}{4q_1^2} \cdot \frac{1}{t_{0.1}} \ln(10Z)$$

Directly under eq. (5), the sentence should read: "Here the coefficient $2\psi(1 + \psi)/(1 + \psi + \psi^2 q_1^2)$ is replaced by Z and the time corresponding to $1 - \bar{E} = 0.1$ by $t_{0.1}$."

POLYMER NEWS

CONFERENCE ON VIBRATIONAL SPECTRA OF HIGH POLYMERS

Milano (Italy) July 18–20, 1963

Industrial Chemistry Department of the Polytechnic,
Piazza L. Da Vinci 32, Milano (Italy)

An important contribution to the progress of the chemistry and physical-chemistry of macromolecules has been given by vibrational spectroscopy and nowadays a growing number of scientists is interested in this experimental and theoretical study of the vibrational spectra of macromolecules particularly those having a stereoregular structure. This conference is under the sponsorship of the Chemistry Committee of the National Research Council of Italy through its National Center for the Chemistry of Macromolecules.

The purpose of the conference is to promote an exchange of ideas among spectroscopists and to review the most recent results, in order to bring up new themes for future research. It is being arranged by a Scientific and Organizing Committee under the direction of Prof. G. B. Bonino and Prof. Giulio Natta.

COLLOQUIUM ON CARBON BLACK

A colloquium on carbon black will be held on September 27 and 28 at the Ecole Supérieure de Chimie de Mulhouse, Mulhouse, France, under the auspices of the Centre National de la Recherche Scientifique. The topics for discussion will be (1) the determination of the structure of carbon black by physical and chemical methods, (2) the oxidation of carbon black, and (3) the reinforcement of rubber and elastomers. The official languages of the meeting will be French, English, and German. Questions concerning this meeting should be directed to Professor J. B. Donnet at Mulhouse.

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